Quantum Mechanics 1

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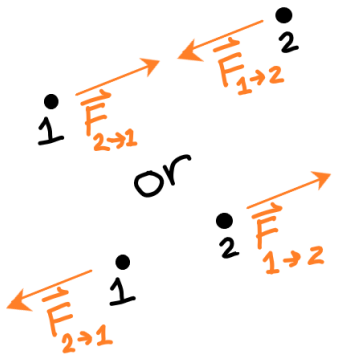
Contents

1 Central Force Problem

1.1 Introduction to the Problem

We start with a system in which there is a force between two objects that depends only on the distance between them and that is directed along the line between them:



$$\vec{F}_{m_2\to m_1} = -\vec{F}_{m_1\to m_{2z}}$$

This vector can be represented as its magnitude in a certain direction $\hat{r}$:

$$\vec{F}_{m_2\to m_1} = f(r)\hat{r}$$

where $\hat{r} = \frac{\vec{r}}{\|\vec{r}\|}$. The magnitude of this force, $f(r)$, is conservative, and is thus the change in potential energy over change in distance, leading to:

$$f(r) = -\frac{dV}{dr}$$

$$\int_0^r f(x)dx = V(r) - V(0)$$

Using Newton's Second Law we can see that:

$$\vec{F}_{m_2\to m_1} = f(r)\hat{r} = m_1\frac{d\vec{r}_1}{dt}$$

$$\vec{F}_{m_1\to m_2} = -f(r)\hat{r} = m_2\frac{d\vec{r}_2}{dt}$$

These two forces are equal and opposite, meaning that:

$$m_1\frac{d\vec{r_1}}{dt} + m_2\frac{d\vec{r_2}}{dt} = 0$$

1.2 Converting to the Center of Mass Frame

We want to use the center of mass. This is because many problems can be simplified using center of mass and it can be conceptualized as "the particle equivalent of a given object for application of Newton's laws of motion." At this point, the weighted relative position of the distributed mass sums to zero and any force can be applied to cause a linear acceleration without an angular acceleration (Wikipedia).

So, finding the center of mass of this system:

$$\vec{r}_{CM} = \frac{m_1\vec{r}_1 + m_2\vec{r}_2}{m_1 + m_2}$$

We can then find the velocity and acceleration of the center of mass:

$$\vec{v}_{CM} = \frac{d}{dt}\vec{r}_{CM} = \frac{1}{m_1 + m_2}[m_1\frac{d\vec{r}_1}{dt} + m_2\frac{d\vec{r}_2}{dt}]$$

$$\vec{a}_{CM} = \frac{d}{dt}\vec{v}_{CM} = \frac{1}{m_1 + m_2}[m_1\frac{d^2\vec{r}_1}{dt^2} + m_2\frac{d^2\vec{r}_2}{dt^2}]$$

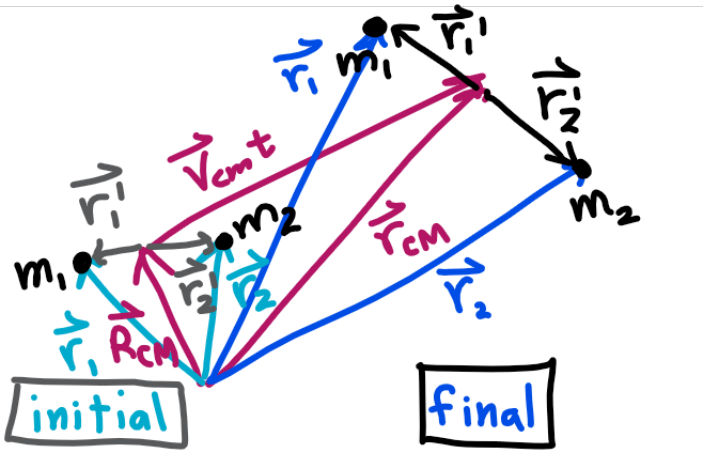
We establish initial conditions of constant velocity $\vec{V}_{CM}$, initial position $\vec{R}_{CM}$, and nonzero angular momentum (this one will come in handy later):

$$\vec{v}_{CM} = \vec{V}_{CM}$$

$$\vec{r}_{CM} = \vec{V}_{CM}t + \vec{R}_{CM}$$

$$\vec{L} \neq 0$$

We can perform a change in coordinates and make the center of mass at time = 0 be our new origin:



$$\vec{r}_1 = \vec{r_1'} + \vec{V}_{CM}t + \vec{R}_{CM}$$
$$\vec{r}_2 = \vec{r_2'} + \vec{V}_{CM}t + \vec{R}_{CM}$$

The acceleration in each coordinate system is the same:

$$\frac{d^2\vec{r}_1}{dt^2} = \frac{d^2\vec{r_1'}}{dt^2}$$
$$\frac{d^2\vec{r}_2}{dt^2} = \frac{d^2\vec{r_2'}}{dt^2}$$

Now we can rewrite the center of mass in the new coordinate system:

$$\vec{r}_{CM} = \frac{m_1\vec{r}_1 + m_2\vec{r}_2}{m_1 + m_2} = \frac{m_1(\vec{r_1'} + \vec{V}_{CM}t + \vec{R}_{CM}) + m_2(\vec{r_2'} + \vec{V}_{CM}t + \vec{R}_{CM})}{m_1 + m_2}$$

$$= \frac{m_1\vec{r_1'} + m_2\vec{r_2'}}{m_1 + m_2} + \frac{\cancel{(m_1 + m_2)}(\vec{V}_{CM}t + \vec{R}_{CM})}{\cancel{m_1 + m_2}}$$

$$= \frac{m_1\vec{r_1'} + m_2\vec{r_2'}}{m_1 + m_2} + \vec{r}_{CM}$$

$$\therefore \frac{m_1\vec{r_1'} + m_2\vec{r_2'}}{m_1 + m_2} = 0$$

From there we make a system of equations and solve for these new position vectors. These position vectors have their origin at the center of mass at $t = 0$:

$$m_1\vec{r_1'} + m_2\vec{r_2'} = 0$$
$$\vec{r_1'} - \vec{r_2'} = \vec{r}$$

$$\vec{r_1'} = \frac{m_2\vec{r}}{m_1 + m_2}$$
$$\vec{r_2'} = \frac{-m_1\vec{r}}{m_1 + m_2}$$

1.3 Finding Angular Momentum

We define reduced mass as follows:

$$m = \frac{m_1 m_2}{m_1 + m_2}$$

If m_1 is small and m_2 is big:

$$\frac{m_1 m_2}{m_1 + m_2} \approx m_1$$

The force in the system (which is the same but in the opposite directions for each of the two objects in the system) can be represented using this reduced mass:

$$\left(\frac{m_1 m_2}{m_1 + m_2}\right)\frac{d^2\vec{r}}{dt^2} = f(r)\hat{r}$$

$$\approx m_1 \frac{d^2\vec{r}}{dt^2} = f(r)\hat{r} = -\frac{dV}{dr}\hat{r}$$

Note that here $\frac{d^2\vec{r}}{dt^2}$ is sometimes termed "relative acceleration" and is the difference in acceleration of the two bodies. It is also, by definition, the acceleration of the distance between the two bodies.

Angular Momentum of this reduced mass system:

$$\vec{L} = \vec{r} \times \vec{p} = m\vec{r} \times \frac{d\vec{r}}{dt}$$

Change in angular momentum over time (should be zero for a closed system):

$$\frac{d\vec{L}}{dt} = m\frac{d\vec{r}}{dt} \times \frac{d\vec{r}}{dt} + m\vec{r} \times \frac{d^2\vec{r}}{dt^2}$$

$$= r\hat{r} \times f(r)\hat{r}$$

$$= rf(r)\hat{r} \times \hat{r} = 0$$

We have proven that the magnitude and direction of the angular momentum $\vec{L}$ don't change over time

1.4 Angular Momentum in Cylindrical Coordinates

Now we can set the direction of the angular momentum as the z direction and choose cylindrical coordinates. This will serve in helping us find additional information about the system, such as angular velocity.

$$\vec{L} = L\hat{z}$$

Cylindrical coordinates are defined as follows:

$$\vec{r} = x\hat{x} + y\hat{y} + z\hat{z} = \rho\hat{\rho} + z\hat{z}$$

$$\hat{\rho} = \cos\phi\hat{x} + \sin\phi\hat{y}$$

$$\hat{\phi} = -\sin\phi\hat{x} + \cos\phi\hat{y}$$

$$\vec{z} = z\hat{z}$$

Conversions:

$$\rho = \sqrt{x^2 + y^2}$$

$$x = \rho\cos\phi$$

$$y = \rho \sin \phi$$

Change over time:

$$\frac{d\hat{\rho}}{dt} = (-\sin\phi\hat{x} + \cos\phi\hat{y})\frac{d\phi}{dt} = \frac{d\phi}{dt}\hat{\phi}$$

$$\frac{d\hat{\phi}}{dt} = (-\cos\phi\hat{x} - \sin\phi\hat{y})\frac{d\phi}{dt} = -\frac{d\phi}{dt}\hat{\rho}$$

$$\frac{d\hat{r}}{dt} = \frac{d\rho}{dt}\hat{\rho} + \rho\frac{d\hat{\rho}}{dt} + \frac{dz}{dt}\hat{z} = \frac{d\rho}{dt}\hat{\rho} + \rho\frac{d\phi}{dt}\hat{\phi} + \frac{dz}{dt}\hat{z}$$

Right-handed system:

$$\hat{\rho} \times \hat{\phi} = \hat{z}$$

$$\hat{\phi} \times \hat{z} = \hat{\rho}$$

$$\hat{z} \times \hat{\rho} = \hat{\phi}$$

Revisiting our equation for angular momentum using cylindrical coordinates:

$$\vec{L} = m(\rho\hat{\rho} + z\hat{z}) \times \left(\frac{d\rho}{dt}\hat{\rho} + \rho\frac{d\phi}{dt}\hat{\phi} + \frac{dz}{dt}\hat{z}\right)$$

$$\vec{L} = L\hat{z} = -mz\rho\frac{d\phi}{dt}\hat{\rho} - m\rho\frac{dz}{dt}\hat{\phi} + m\rho^2\frac{d\phi}{dt}\hat{z} + mz\frac{d\rho}{dt}\hat{\phi}$$

All terms not in the $\hat{z}$ direction must be zero because of the direction we defined the angular momentum, therefore:

$$\vec{L} = L\hat{z} = \cancel{-mz\rho\frac{d\phi}{dt}\hat{\rho}} - \cancel{m\rho\frac{dz}{dt}\hat{\phi}} + m\rho^2\frac{d\phi}{dt}\hat{z} + \cancel{mz\frac{d\rho}{dt}\hat{\phi}}$$

$$L\hat{z} = m\rho^2\frac{d\phi}{dt}\hat{z}$$

The value of L is therefore:

$$L = m\rho^2\frac{d\phi}{dt}$$

Since we defined our system as having a nonzero, constant angular momentum, we can now infer that m, ρ^2 and $\frac{d\phi}{dt}$ must all be nonzero.

Additionally, rearranging:

$$\frac{d\phi}{dt} = \frac{L}{m\rho^2}$$

$\frac{d\phi}{dt}$ is the change in angle over time, otherwise known as the angular velocity, often denoted ω.

1.5 Finding Total Energy Equation from Total Force

Given that the angular momentum is in the z-direction, we can infer that the two bodies must exist on the xy plane, and thus the position and force of the reduced mass system would be:

$$\vec{r} = \rho\hat{\rho}$$
$$f(r) = f(\rho)$$

In order to find a value for the force in cylindrical coordinates, we start by first finding the second derivative of $\vec{r}$:

$$\frac{d^2\vec{r}}{dt^2} = \frac{d}{dt}\left(\frac{d\hat{r}}{dt}\right) = \frac{d}{dt}\left(\frac{d\rho}{dt}\hat{\rho} + \rho\frac{d\phi}{dt}\hat{\phi} + \frac{dz}{dt}\hat{z}\right)$$

$$= \frac{d^2\vec{\rho}}{dt^2} = \frac{d^2\rho}{dt^2}\hat{\rho} + \frac{d\rho}{dt}\frac{d\phi}{dt}\hat{\phi} + \frac{d^2\phi}{dt^2}\hat{\phi} - \rho\left(\frac{d\phi}{dt}\right)^2\hat{\rho}$$

$$= \left(\frac{d^2\rho}{dt^2} - \rho\left(\frac{d\phi}{dt}\right)^2\right)\hat{\rho} + \left(2\frac{d\rho}{dt}\frac{d\phi}{dt} + \rho\frac{d^2\phi}{dt^2}\right)\hat{\phi}$$

If we take the derivative of the angular momentum with respect to time it can add valuable information for simplifying this equation. We use the value for angular momentum previously found:

$$L\hat{z} = m\rho^2\frac{d\phi}{dt}\hat{z}$$

$$\frac{d\vec{L}}{dt} = 0$$

$$\frac{d\vec{L}}{dt} = \frac{d}{dt}\left(m\rho^2\frac{d\phi}{dt}\right)\hat{z}$$

$$= \rho\left(2\frac{d\rho}{dt}\frac{d\phi}{dt} + \rho\frac{d^2\phi}{dt}\right)\hat{z}$$

Since we know ρ cannot be 0 (from the angular momentum equation), then:

$$2\frac{d\rho}{dt}\frac{d\phi}{dt} + \rho\frac{d^2\phi}{dt} = 0$$

Therefore going back to the second derivative of $\vec{r}$ we get:

$$\frac{d^2\vec{r}}{dt^2} = \left(\frac{d^2\rho}{dt^2} - \rho\left(\frac{d\phi}{dt}\right)^2\right)\hat{\rho}$$

The value of the force thus becomes:

$$f(\rho) = m\left(\frac{d^2\rho}{dt^2} - \rho\left(\frac{d\phi}{dt}\right)^2\right) = \frac{-dV(\rho)}{d\rho}$$

Rearranging and multiplying by $\frac{d\rho}{dt}$:

$$\frac{d\rho}{dt}\left[m\left(\frac{d^2\rho}{dt^2}-\rho\left(\frac{d\phi}{dt}\right)^2\right)+\frac{dV(\rho)}{d\rho}=0\right]$$

$$m\frac{d^2\rho}{dt^2}\frac{d\rho}{dt}-\frac{L^2}{m}\frac{1}{\rho^3}\frac{d\rho}{dt}+\frac{dV(\rho)}{d\rho}\frac{d\rho}{dt}=0$$

$$\frac{d}{dt}\left(\frac{1}{2}m\left(\frac{d\rho}{dt}\right)^2\right)+\frac{d}{dt}\left(\frac{L^2}{2m\rho^2}\right)+\frac{dV(\rho)}{dt}=0$$

What we're left with is an equation for the total energy differentiated with respect to time:

$$\frac{d}{dt}\left[\frac{1}{2}m\left(\frac{d\rho}{dt}\right)^2+\left(\frac{L^2}{2m\rho^2}\right)+dV(\rho)\right]=0$$

$$\frac{d}{dt}\left(Linear\,Kinetic\,Energy+Angular\,Kinetic\,Energy+Potential\,Energy\;=Total\,Energy\right)=0$$

1.6 General Example

Now we can examine a general example of the Central Force Problem where k is some force/energy constant and $V(\rho)$ is some potential energy:

$$V(\rho)=\frac{-k}{\rho}$$

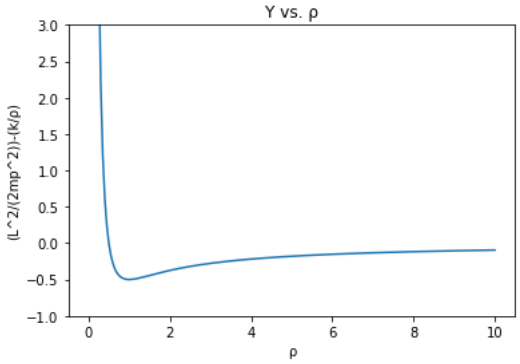
$$\frac{dV}{d\rho}=\frac{k}{\rho^2}$$

$$F=\frac{-dV}{d\rho}=\frac{-k}{\rho^2}$$

Re-examining the total energy equation:

$$E_{total}=\frac{1}{2}m\left(\frac{d\rho}{dt}\right)^2+\left(\frac{L^2}{2m\rho^2}\right)+V(\rho)$$

We can plot the part of this equation that corresponds to angular kinetic energy and potential energy ($\left(L^2/2m\rho\right)+V(\rho)$) with respect to ρ. Remember ρ is the same as r or distance for our given initial conditions.



This part of the equation that we have plotted is dependent on k (our force/energy constant), on the angular momentum L, and on the mass m. The graph shown has these values set to 1. On the other hand, the linear kinetic energy is not dependent on L or k. Furthermore, if we rearrange we get:

$$Y_{min} \leq \frac{L^2}{2m\rho^2} - \frac{k}{\rho} = E - \frac{1}{2}m\left(\frac{d\rho}{dt}\right)^2$$

$$E \geq \frac{1}{2}m\left(\frac{d\rho}{dt}\right)^2 + Y_{min}$$

$$E \geq Y_{min}$$

Therefore Y_{min} (the lowest Y-value in the graph) is the minimum total energy which we will call E_{min}

And how do we find this E_{min}? We can take the derivative of the graph and set it to 0 to find the minimum.

$$\frac{dY}{dp} = \frac{-L^2}{m\rho^3} + \frac{k}{\rho^2} = 0$$

$$\implies \frac{L^2}{m\rho^{\cancel{3}}} = \frac{k}{\rho^2}$$

$$\implies L^2 = km\rho$$

$$\implies L = \sqrt{km\rho}$$

And so we end up with an expression for angular momentum L at the point where there is a stable, circular orbit.

1.7 Earth and Sun

We are going to focus once more on the previously graphed quantity $\frac{L^2}{2m\rho} - \frac{k}{\rho}$ which corresponds physically to the sum of the angular kinetic energy and the potential energy and can tell us about the minimum total energy. We'll call this

value Y. We are going to set our k constant equal to Gm_Sm_E where G is the gravitational constant m_S and m_E are the masses of the Sun and Earth.

$$Y = \left(\frac{L^2}{2m\rho^2}\right) - \frac{Gm_Sm_E}{\rho}$$

We know that there should be no change in the minimum energy over distance so:

$$\frac{dY_{min}}{d\rho} = \frac{-2L^2}{2m\rho^3} + \frac{Gm_Sm_E}{\rho^2} = 0$$

$$\frac{1}{\rho_{min}^2}\left[Gm_Sm_E - \frac{L^2}{m\rho_{min}^2}\right] = 0$$

$$Gm_Sm_E = \frac{L^2}{m\rho_{min}}$$

Therefore:

$$L^2 = m\rho_{min}Gm_Sm_E$$

$$\rho_{min} = \frac{L^2}{Gm_Sm_Em}$$

As you may remember, m is the reduced mass of the system. For a system such as the Sun and Earth, this can be approximated as solely the mass of the much smaller object, in this case the Earth:

$$m \approx m_E$$

$$L^2 \approx \rho_{min}Gm_Sm_E^2$$

$$\rho_{min} \approx \frac{L^2}{Gm_Sm_E^2}$$

Substituting L^2 and ρ_{min} back into our minimum energy equation we get:

$$Y_{min} = E_{min} = \frac{\cancel{\rho_{min}}Gm_Sm_E\cancel{^2}}{2\cancel{m_E}\rho_{min}\cancel{^2}} - \frac{Gm_Sm_E}{\rho_{min}}$$

$$E_{min} = \frac{Gm_Sm_E}{2\rho_{min}} - \frac{Gm_Sm_E}{\rho_{min}} = \frac{-Gm_Sm_E}{2\rho_{min}}$$

$$E_{min} = \frac{-Gm_Sm_E}{2}\left[\frac{Gm_Sm_E^2}{L^2}\right] = \frac{-G^2m_S^2m_E^3}{2L^2}$$

In order to find the minimum energy we must go back to our equations for angular momentum L:

$$L = m\rho^2\frac{d\phi}{dt}$$

$$L = \sqrt{km\rho}$$

In this case our k constant is Gm_Sm_E.
So if we substitute our values for the Earth and Sun:

$$\rho = 1.496 \times 10^{11}\ meters$$
$$G = 6.67 \times 10^{-11}\ N * kg^{-2}m^2$$
$$m_S = 1.9891 \times 10^{30}\ kg$$
$$m_E = 5.97219 \times 10^{24}\ kg$$

$$L = \sqrt{Gm_Sm_E^2\rho} = 2.66 \times 10^{40} \frac{kg * m^2}{s}$$

We can also do the same for the angular velocity $\frac{d\phi}{dt}$:

$$\frac{d\phi}{dt} = \frac{L}{m_E\rho^2} = 1.991 \times 10^{-7}\ sec^{-1}$$

The amount of time it takes for the Earth to go around the Sun would then be:

$$P = \frac{d\phi}{dt} * \frac{31,536,000\ sec * year^{-1}}{2\pi} = 0.999\ years \approx 1\ year$$

We can also go back and find the minimum energy of the system in this circular orbit:

$$E_{min} = \frac{-G^2m_S^2m_E^3}{2L^2} = 2.65 \times 10^{-39}\ J$$

1.8 Bohr Atom

Now we'll examine a hydrogenic atom, meaning any atom with a nucleus and 1 electron orbiting it. We'll set the k constant equal to $\frac{Ze^2}{4\pi\epsilon_0\rho}$ where e is the charge of an electron, Ze is the charge of the protons in the nucleus where Z is the number of protons, and $\frac{1}{4\pi\epsilon_0}$ is the constant for the permittivity of free space

$$Y = \left(\frac{L^2}{2m\rho}\right) - \frac{Ze^2}{4\pi\epsilon_0\rho}$$

We know that there should be no change in the minimum energy over distance so:

$$\frac{dY_{min}}{d\rho} = \frac{-2L^2}{2m\rho^3} + \frac{Ze^2}{4\pi\epsilon_0\rho^2} = 0$$
$$\frac{1}{\rho_{min}^2}\left[\frac{Ze^2}{4\pi\epsilon_0} - \frac{L^2}{m\rho_{min}^2}\right] = 0$$
$$\frac{Ze^2}{4\pi\epsilon_0} = \frac{L^2}{m\rho_{min}}$$

Therefore:

$$L^2 = \frac{m\rho_{min}Ze^2}{4\pi\epsilon_0}$$

$$\rho_{min} = \frac{L^2 4\pi\epsilon_0}{Ze^2 m}$$

Substituting this back into the minimum energy equation we get:

$$E_{min} = \frac{\cancel{m}\cancel{\rho_{min}}Ze^2}{2\cancel{m}\cancel{\rho_{min}}^2} - \frac{Ze^2}{4\pi\epsilon_0\rho_{min}}$$

$$E_{min} = \frac{Ze^2}{8\pi\epsilon_0\rho_{min}} - \frac{Ze^2}{4\pi\epsilon_0\rho_{min}} = \frac{-Ze^2}{8\pi\epsilon_0\rho_{min}}$$

$$E_{min} = \frac{-Ze^2}{8\pi\epsilon_0}\left[\frac{Ze^2 m}{L^2 4\pi\epsilon_0}\right] = \frac{-Z^2e^4m}{2(4\pi\epsilon_0)^2}\frac{1}{L^2}$$

$$E_{min} = \frac{-Z^2e^4m4\pi^2}{2(4\pi\epsilon_0)^2h^2}\frac{1}{n^2} = \frac{-Z^2e^4m}{8\epsilon_0^2h^2}\frac{1}{n^2}$$

However, the minimum energy of a Bohr atom is quantized through its angular momentum L (where n is an integer):

$$L = \frac{h}{2\pi}n$$

But where did this value for the angular momentum come from? Well, when Niels Bohr analyzed hydrogen spectrum data, he noticed that the angular momentum must be quantized in order to fit the data he gathered. De Broglie expanded on this by justifying this quantization using the De Broglie relation, $p = \frac{h}{\lambda}$ which basically implies that the electron has a wave-like nature and thus a wavelength that relates to its momentum p.

If we assume the electron orbits that nucleus in a standing wave, where only integers of that standing wave frequency can exist along the orbit, $2\pi r$, then we can justify the following:

$$2\pi r = n\lambda$$

Using the De Broglie relation:

$$2\pi r = n\frac{h}{p}$$

Finally, through some rearranging we arrive once more at the quantized angular momentum:

$$\frac{h}{2\pi}n = pr = L$$

For the smallest value of n, n=1, we can find the angular momentum and minimum energy:

$$L = \frac{h}{2\pi} * 1 = 1.05457 \times 10^{-34}\ J * sec$$

$$m_{e^-} = 9.1093837 \times 10^{-31}\ kg$$

$$E_{min} = \frac{-Z^2 e^4 m}{8\epsilon_0^2 h^2} \frac{1}{n^2} = -2.179 \times 10^{-18}\ J = -13.607\ eV$$

2 Wave Mechanics

A general solution to the one dimensional classical wave equation is:

$$\psi(x,t) = e^{i(kx-\omega t)}$$

$kx - \omega t$ is a constant so we can see:

$$c = kx - \omega t$$

Focusing on the x in this equation:

$$x = \frac{c}{k} + \frac{\omega t}{k}$$

Since c, k (wavenumber), and ω (angular frequency) are all constant, this is an equation of the position that is dependent on $\frac{\omega}{k}$, which is the velocity of the wave:

$$0 = kdx - \omega dt$$

$$\frac{dx}{dt} = \frac{\omega}{k} = \frac{2\pi f}{\frac{2\pi}{\lambda}} = \lambda f = v$$

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Particle mechanics Energy

$$E_{total} = \frac{1}{2}m\left(\frac{d\rho}{dt}\right)^2 + \left(\frac{L^2}{2m\rho^2}\right) + V(\rho)$$

$$E = \frac{\vec{p}\cdot\vec{p}}{2m} + V$$

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In wave mechanics, the process of finding the total energy (or extracting other information such as average position) is different than in particle mechanics. We have to perform an operation on the wave function that yields the total energy multiplied by the original wave function:

$$(energy\,operator)\psi = \hat{H}\psi = E_{total}\psi$$

$$(operator)\psi = (information)\psi$$

2.1 Energy and Momentum Operators

Some operations we can perform on this wave:

$$i\hbar\frac{d}{dt}(\psi(x,t)) = \hbar\omega\psi(x,t)$$

where $i\hbar\frac{d}{dt}$ is the energy operator and $\hbar\omega$ is the resulting value for energy.

$$-i\hbar\frac{d}{dx}(\psi(x,t)) = \hbar k\psi(x,t)$$

where $-i\hbar\frac{d}{dx}$ is the momentum operator and $\hbar k$ is the resulting value for momentum.

Therefore energy and momentum of a wave are:

$$E = \hbar\omega$$
$$p = \hbar k$$

This makes sense when examining some possible units of each:

$$E = \hbar\omega = (J * sec)(sec^{-1}) = J$$
$$p = \hbar k = (J * sec)(m^{-1}) = ((\frac{kg * m^2}{sec^2}) * sec)(\frac{1}{m}) = kg * \frac{m}{sec}$$

We can also rewrite the angular frequency and energy of a free wave using our values for energy and momentum:

$$p = \hbar k$$
$$E = \hbar\omega = \frac{p^2}{2m}$$
$$\implies E = \frac{\hbar^2 k^2}{2m}$$
$$\implies \omega = \frac{\hbar k^2}{2m}$$

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Experimental Input

Through various types of measurement, we obtain values at certain locations that we interpret as the intensity of this wave function, and we represent them as the square of the wave function:

$$P(x) = \psi^2(x)$$

*If we assume $\psi(x) > 0$, then for all x, $\psi(x) = \sqrt{P(x)}$

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2.2 Understanding Time-Independent Free Wave

Free waves must be proportional to this general solution, $e^{i(kx-\omega t)}$.

Now, for the wave at time=0 and setting the proportionality constant between ψ and $e^{i(kx-\omega t)}$ equal to 1:

$$\psi(x) = e^{ikx}$$

This wave function can be represented as the sum of many different wave functions at different frequencies (Fourier Transform or visually interpreted as an infinite vector summation). But how do we know this is true? We are going to go through the steps to prove it:

$$\psi(x) = \int_{-\infty}^{\infty} \tilde{\psi}(k) e^{ikx} dk$$

First, we'll set up some parameters for this free wave, and assume that the function starts and ends at the same value (this makes it periodic, and thus we can later represent it as a Fourier series). Although we are denoting a length for our function, eventually this length should be extended to approach infinity:

$$x = \left[\frac{-L}{2}, \frac{L}{2}\right]$$

$$\psi\left(\frac{-L}{2}\right) = \psi\left(\frac{L}{2}\right)$$

$$\implies e^{i(-k(\frac{L}{2}))} = e^{i(k\frac{L}{2})}$$

$$\implies \frac{1}{e^{i(k(\frac{L}{2}))}} = e^{i(k\frac{L}{2})}$$

$$\implies e^{i(kL)} = 1 = e^{i2\pi n}$$

Therefore:

$$kL = 2\pi n$$

$$\psi(x) = e^{i\frac{2\pi n}{L}x}$$

*Note, the intensity, which we had previously described as the $\psi(x)^2$ is more accurately $\psi^*(x)\psi(x)$.

Kronecker Delta for a Free Wave

Now, we are going to define a function in this bound, called $g_n(x)$, with a constant $\frac{1}{\sqrt{L}}$ that will serve when normalizing the entire wave function to have a total intensity of 1 along the entirety of L:

$$g_n(x) = \frac{1}{\sqrt{L}} e^{i\frac{2\pi n}{L}x}$$

If we multiply the function by its complex conjugate and integrate from $\frac{-L}{2}$ to $\frac{L}{2}$:

$$\int_{\frac{-L}{2}}^{\frac{L}{2}} g_n^*(x) g_l(x) dx = \frac{1}{L} \int_{\frac{-L}{2}}^{\frac{L}{2}} e^{i\frac{2\pi}{L}(l-n)x} dx$$

$$= \frac{1}{L} * [L \; if \; l = n, 0 \; if \; l \neq n]$$

$$= \frac{L}{L} \delta_{nl} = \delta_{nl}$$

This symbol δ_{nl} is called the Kronecker Delta and is a representation of the result where all values equal 0 except for when $n = l$. When $n = l$, the Kronecker Delta denotes a value of 1.

Finding a Specific Coefficient/Component of Our Wave Function

Since our function $\psi(x)$ is periodic, we can rewrite $\psi(x)$ as a Fourier Series, in terms of a linear combination of $\bar{\psi}_n g_n(x)$:

$$\psi(x) = \sum_{n=-\infty}^{\infty} \tilde{\psi}_n g_n(x)$$

Multiplying by $g_l^*(x)$ and integrating (and taking out the $\frac{1}{\sqrt{L}}$ from $g_l^*(x)$ for better notation):

$$\frac{1}{\sqrt{L}} \int_{\frac{-L}{2}}^{\frac{L}{2}} \psi(x) g_l^*(x) dx = \frac{1}{L} \int_{\frac{-L}{2}}^{\frac{L}{2}} \sum_{n=-\infty}^{\infty} \tilde{\psi}_n g_n(x) g_l^*(x) dx$$

$$= \frac{1}{L} \sum_{n=-\infty}^{\infty} \tilde{\psi}_n \int_{\frac{-L}{2}}^{\frac{L}{2}} g_n(x) g_l^*(x) dx = \frac{1}{L} \sum_{n=-\infty}^{\infty} \tilde{\psi}_n \delta_{nl}$$

$$= \frac{1}{L} \tilde{\psi}_{n=l}$$

Therefore, when we multiply the wave function by the complex conjugate of the function and then integrate, we end up with the that "component" of the wave function (and maybe also with some coefficient depending on our notation):

$$\implies \tilde{\psi}_l = \int_{\frac{-L}{2}}^{\frac{L}{2}} \psi(x) g_l^*(x) dx = \int_{\frac{-L}{2}}^{\frac{L}{2}} \psi(x) e^{-i\frac{2\pi l}{L}} x dx$$

Going to infinite length

Now that we have defined the wave function in both position and wave number domains across L, we want to extend that to infinite length.

So, once more we can examine our function as a Fourier Series (Reminder that we can do so because we expressly had defined it as periodic by making $\psi(\frac{-L}{2}) = \psi(\frac{L}{2})$).

This time removing $\frac{1}{L}$ for notation purposes:

$$\psi(x) = \sum_{n=-\infty}^{\infty} \tilde{\psi}_n g_n(x) = \frac{1}{L} \sum_{n=-\infty}^{\infty} \tilde{\psi}_n e^{i(\frac{2\pi}{L})nx}$$

We can rewrite this in the format of a Riemann Sum:

$$\psi(x) = \frac{1}{2\pi} \sum_{n=-\infty}^{\infty} \left(\frac{2\pi}{L}\right) \tilde{\psi}_n e^{i(\frac{2\pi}{L})nx}$$

****

(Riemann Sum Formula for Reference):

$$\lim_{\Delta \to \infty} \sum_{n=-\infty}^{\infty} \Delta \tilde{f}\left(n\Delta\right) = \int_{-\infty}^{\infty} \tilde{f}(x)$$

****

Previously we said that $kL = 2\pi n$. Now, denoting $k = \frac{2\pi}{L}$, and as L approaches ∞ we get $\psi(x)$ written as an inverse Fourier transform:

$$\psi(x) = \frac{1}{2\pi} \int_{-\infty}^{\infty} \tilde{\psi}(k) e^{ikx} dk$$

Proving that the above is true:

$$\psi(x) = \frac{1}{2\pi} \int_{-\infty}^{\infty} \left[\int_{-\infty}^{\infty} \psi(y) e^{-iky} dy \right] e^{ikx} dk$$

$$\psi(x) = \int_{-\infty}^{\infty} \psi(y) \left[\int_{-\infty}^{\infty} \frac{1}{2\pi} e^{ik(x-y)} dk \right] dy$$

$$= \int_{-\infty}^{\infty} \psi(y) \left[\delta(x-y)\right] dy$$

****

Dirac Delta Function: :

$$\delta(x-y) = \delta(z) = \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{ikz} dk$$

****

Tying back to measurements

Taking a look at our measurements (or really the measurements that someone, somewhere took), they appear in a Gaussian distribution so we can define P(x) as such:

$$P(x) = \frac{1}{\sigma\sqrt{2\pi}} e^{-\frac{x^2}{2\sigma^2}}$$

To solve the integral of this across all of x we can examine this known integral solution:

$$\int_{-\infty}^{\infty} e^{-\alpha x^2} dx = \sqrt{\frac{\pi}{\alpha}}$$

Relating it back to the Gaussian Distribution:

$$\int_{-\infty}^{\infty} P(x) = \int_{-\infty}^{\infty} \frac{1}{\sigma\sqrt{2\pi}} e^{-\frac{x^2}{2\sigma^2}} dx = 1$$

The wave function defined in terms of this Gaussian distribution :

$$\psi(x) = \frac{1}{(2\pi\sigma^2)^{\frac{1}{4}}} e^{-\frac{x^2}{4\sigma^2}}$$

We can again perform a Fourier Transform on this to find a different domain of this function (domain k) :

$$\bar{\psi}(k) = \frac{1}{(2\pi\sigma^2)^{\frac{1}{4}}} \int_{-\infty}^{\infty} e^{-\frac{x^2}{4\sigma^2} - ikx} dx$$

$$= \frac{1}{(2\pi\sigma^2)^{\frac{1}{4}}} \int_{-\infty}^{\infty} e^{-\frac{1}{4\sigma^2}[x^2 + 4\sigma^2 ikx]} dx$$

$$= \frac{1}{(2\pi\sigma^2)^{\frac{1}{4}}} \int_{-\infty}^{\infty} e^{-\frac{1}{4\sigma^2}[(x+2\sigma^2 ik)^2 + 4\sigma^4 k^2]} dx$$

$$\bar{\psi}(k) = \frac{1}{(2\pi\sigma^2)^{\frac{1}{4}}} e^{-\sigma^2 k^2} \int_{-\infty}^{\infty} e^{-\frac{1}{4\sigma^2}(x+2\sigma^2 ik)^2} dx$$

Now a change of variables:

$$z = x + 2i\sigma^2 k$$

$$\bar{\psi}(k) = \frac{1}{(2\pi\sigma^2)^{\frac{1}{4}}} e^{-\sigma^2 k^2} \int_{-\infty+2i\sigma^2 k}^{\infty+2i\sigma^2 k} e^{-\frac{1}{4\sigma^2} z^2} dz$$

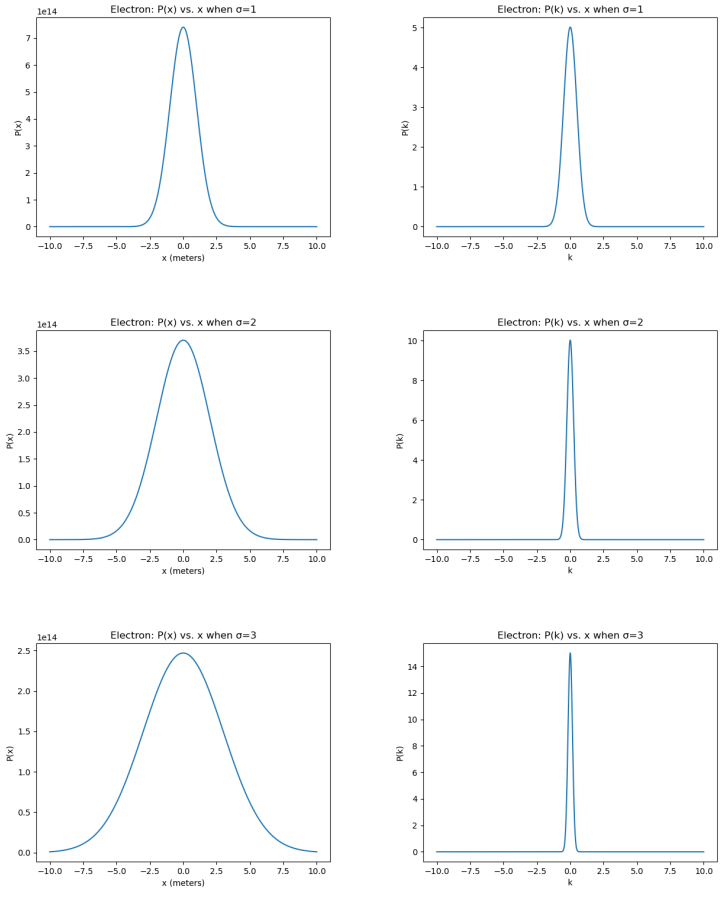
Now through Cauchy's Theorem this becomes:

$$\bar{\psi}(k) = \frac{1}{(2\pi\sigma^2)^{\frac{1}{4}}} e^{-\sigma^2 k^2} \int_{-\infty}^{\infty} e^{-\frac{1}{4\sigma^2} z^2} dz = \frac{1}{(2\pi\sigma^2)^{\frac{1}{4}}} e^{-\sigma^2 k^2} \sqrt{4\sigma^2 \pi}$$

$$\bar{\psi}(k) = 2^{\frac{3}{4}} \pi^{\frac{1}{4}} \sigma^{\frac{1}{2}} e^{-\sigma^2 k^2}$$

$$P(k) = (\bar{\psi}(k))^2 = 2^{\frac{3}{2}} \pi^{\frac{1}{2}} \sigma e^{-2\sigma^2 k^2}$$

We can look at the probability distributions in both position and wavenumber domains for different standard deviations and notice that as one spreads, the other narrows:



2.3 Understanding Time-Dependent Free Wave in the Position (x) Domain

Our next goal is to find $\psi(x,t)$ for a free wave.

From the general solution:

$$e^{i(kx-\omega t)} = e^{ikx}e^{\frac{-i\hbar k^2}{2m}t}$$

Also, our new value of $\bar{\psi}(k)$ from the Gaussian distribution of $P(x)$ is:

$$\bar{\psi}(k) = 2^{\frac{3}{4}}\pi^{\frac{1}{4}}\sigma^{\frac{1}{2}}e^{-\sigma^2 k}$$

We can take the Fourier transform of $\bar{\psi}(k,t)$ to find $\psi(x,t)$:

$$\psi(x,t) = \int_{-\infty}^{\infty}\bar{f}(k)e^{i(kx-\omega t)}dk = \int_{-\infty}^{\infty}\frac{2^{\frac{3}{4}}\pi^{\frac{1}{4}}\sigma^{\frac{1}{2}}}{2\pi}e^{-\sigma^2k^2}e^{ikx}e^{\frac{-i\hbar k^2}{2m}t}dk$$

$$= \int_{-\infty}^{\infty}\frac{2^{\frac{3}{4}}\pi^{\frac{1}{2}}\sigma^{\frac{1}{2}}}{2\pi}e^{-\sigma^2k^2}e^{ikx}e^{\frac{-i\hbar k^2}{2m}t}dk = \int_{-\infty}^{\infty}\frac{2^{\frac{3}{4}}\pi^{\frac{1}{2}}\sigma^{\frac{1}{2}}}{2\pi}e^{-\sigma^2k^2\frac{-i\hbar k^2}{2m}t+ikx}dk$$

$$= \int_{-\infty}^{\infty}\frac{2^{\frac{3}{4}}\pi^{\frac{1}{2}}\sigma^{\frac{1}{2}}}{2\pi}e^{-(\sigma^2k^2+\frac{i\hbar t}{2m}k^2)+ikx}dk = \int_{-\infty}^{\infty}\frac{2^{\frac{3}{4}}\pi^{\frac{1}{2}}\sigma^{\frac{1}{2}}}{2\pi}e^{-(\sigma^2+\frac{i\hbar t}{2m})[k^2-\frac{ik}{\sigma^2+\frac{i\hbar t}{2m}}x]}dk$$

$$= \int_{-\infty}^{\infty}\frac{2^{\frac{3}{4}}\pi^{\frac{1}{2}}\sigma^{\frac{1}{2}}}{2\pi}e^{-(\sigma^2+\frac{i\hbar t}{2m})[k^2-\frac{ik}{\sigma^2+\frac{i\hbar t}{2m}}x]}dk = \int_{-\infty}^{\infty}\frac{2^{\frac{3}{4}}\pi^{\frac{1}{2}}\sigma^{\frac{1}{2}}}{2\pi}e^{-(\sigma^2+\frac{i\hbar t}{2m})[k-\frac{ix}{2(\sigma^2+\frac{i\hbar t}{2m})}+\frac{x^2}{4(\sigma^2+\frac{i\hbar t}{2m})^2}]}dk$$

$$= \frac{2^{\frac{3}{4}}\pi^{\frac{1}{2}}\sigma^{\frac{1}{2}}}{2\pi}\frac{\pi^{\frac{1}{2}}}{[\sigma^2+\frac{i\hbar t}{2m}]^{\frac{1}{2}}}e^{-\frac{x^2}{4(\sigma^2+\frac{i\hbar t}{2m})}} = \left[\frac{\sigma^2}{2\pi(\sigma^2+\frac{i\hbar t}{2m})^2}\right]^{\frac{1}{4}}e^{-\frac{x^2}{4(\sigma^2+\frac{i\hbar t}{2m})}}$$

$$\psi(x,t) = \left[\frac{\sigma^2}{2\pi(\sigma^2+\frac{i\hbar t}{2m})^2}\right]^{\frac{1}{4}}e^{-\frac{x^2}{4(\sigma^2+\frac{i\hbar t}{2m})}}$$

$$P(x,t) = \psi(x,t)\psi^*(x,t) = \frac{\sigma}{\sqrt{2\pi}(\sigma^2+\frac{i\hbar t}{2m})^{\frac{1}{4}}}e^{-\frac{x^2}{4}\left(\frac{1}{\sigma^2+\frac{i\hbar t}{2m}}+\frac{1}{\sigma^2-\frac{i\hbar t}{2m}}\right)}$$

$$= \frac{1}{\sqrt{2\pi\sigma^2(1+\frac{\hbar^2t^2}{4m^2\sigma^4})}}e^{\frac{-x^2}{2\sigma^2}\left(\frac{1}{1+\frac{\hbar^2t^2}{4m^2\sigma^4}}\right)}$$

$$P(x,t) = \frac{1}{\sqrt{2m(\sigma(t))^2}}e^{\frac{x^2}{2(\sigma(t))^2}}$$

$$\sigma(t) = \sigma\sqrt{1+\frac{\hbar^2t^2}{4m^2\sigma^4}}$$

****

What we've established so far:

For a Gaussian Distribution of Intensities:

$$\psi(x) = \frac{1}{(2\pi\sigma^2)^{\frac{1}{4}}} e^{-\frac{x^2}{4\sigma^2}}$$

$$\bar{\psi}(k) = 2^{\frac{3}{4}} \pi^{\frac{1}{2}} \sigma^{\frac{1}{2}} e^{-\sigma^2 k^2}$$

$$P(x) = \frac{1}{\sqrt{2\pi\sigma^2}} e^{-\frac{x^2}{2\sigma^2}}$$

$$\implies \psi(x,0) = \frac{1}{(2\pi\sigma^2)^{\frac{1}{4}}} e^{-\frac{x^2}{4\sigma^2}} = \psi(x)$$

$$[\psi(x,0)]^2 = P(x,0)$$

$$\psi(x,t) = \left[\frac{\sigma^2}{2\pi(\sigma^2 + \frac{i\hbar t}{2m})^2}\right]^{\frac{1}{4}} e^{-\frac{x^2}{4(\sigma^2 + \frac{i\hbar t}{2m})}}$$

$$P(x,t) = \frac{1}{\sqrt{2m(\sigma(t))^2}} e^{\frac{x^2}{2(\sigma(t))^2}}$$

$$\sigma(t) = \sigma\sqrt{1 + \frac{\hbar^2 t^2}{4m^2\sigma^4}}$$

$$P(x,0) = \frac{1}{\sqrt{2\pi\sigma^2}} e^{-\frac{x^2}{2\sigma^2}}$$

$$\implies \psi(x,0) = \frac{1}{(2\pi\sigma^2)^{\frac{1}{4}}} e^{-\frac{x^2}{4\sigma^2}} = \psi(x)$$

Small Review on Types of Operations Used

For x: $[\frac{-L}{2}, \frac{L}{2}]$ we previously established:

$$g_n(x) = \frac{1}{\sqrt{L}} e^{i\frac{2\pi n x}{L}}$$

This $g_n(x)$ is defined as a complete orthonormal set.

$$\int_0^\infty g_l^*(x) g_n(x) dx = \delta_{ln}$$

$$f(x) = \sum_{n=0}^{\infty} \tilde{f}_n g_n(x)$$

If L $\to \infty$

$$\implies \tilde{f}_n = \sqrt{L} \int_{\frac{-L}{2}}^{\frac{L}{2}} f(x) g_n^*(x) dx$$

(This is a Riemann Sum, $\Delta = \frac{2\pi}{l} \to$ integral)

$$\tilde{f}(k) = \int_{\infty}^{\infty} f(x) e^{-ikx} dx, \;\; f(x) = \frac{1}{2\pi} \int_{\infty}^{\infty} \tilde{f}(k) e^{ikx} dk$$

$$\delta(x) = \frac{1}{2\pi} \int_{\infty}^{\infty} e^{ikx} dk$$

****

2.4 Characteristic Time

Standard deviation over the course of time is:

$$\sigma(t) = \sigma \sqrt{1 + \frac{\hbar^2 t^2}{m^2 \sigma^4}} = \sigma \sqrt{1 + \tau^2}$$

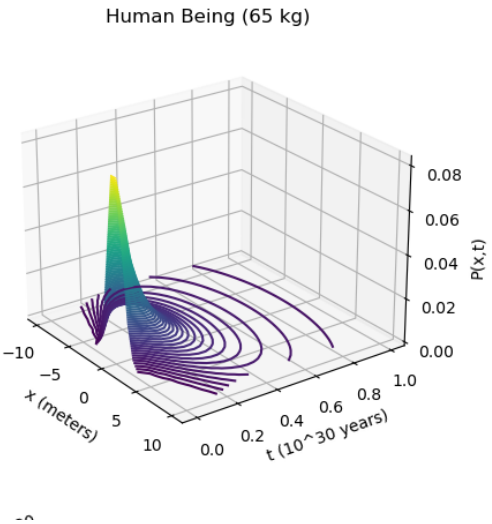
$$\tau = \frac{\hbar t}{m\sigma^2} = \frac{t}{(\frac{m\sigma^2}{\hbar})} = \frac{t}{T}$$

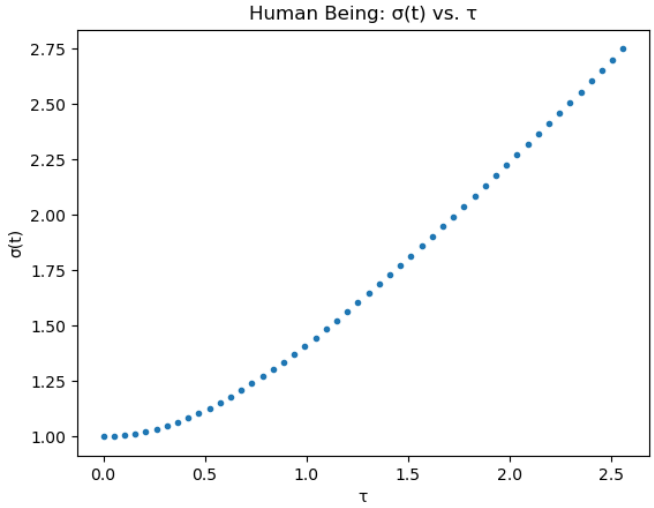
T is the characteristic time. It depends on accuracy and mass and is used for comparison between objects/systems.

2.5 Examples of Various Gaussian Distribution Decays

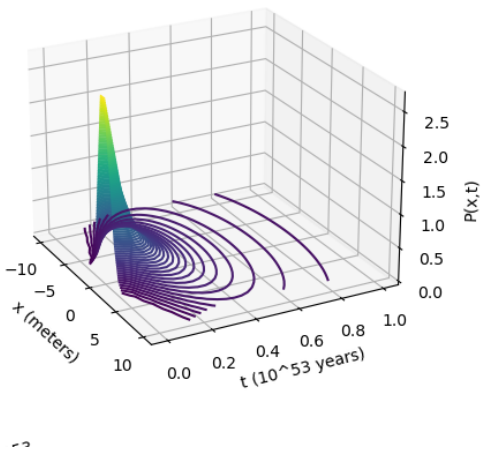
**Note, for all of the following calculations and graphs, $\sigma = 1$ (σ is $\sigma(t)$ at t=0)

It would take a human being $(the\ age\ of\ the\ universe)^3$ time in order to really decay into nothingness:

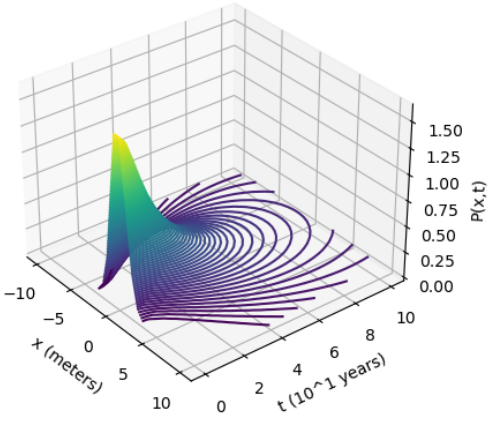


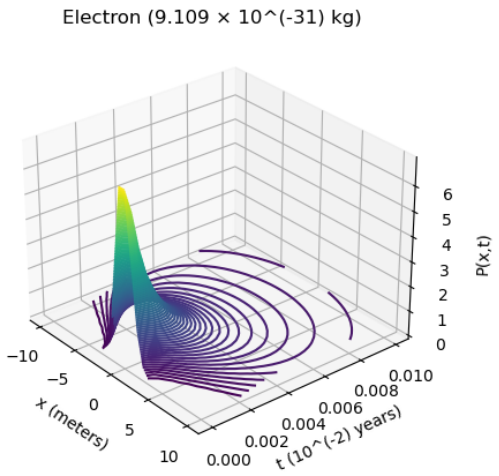


Earth (5.97219 x 10^24 kg)



Neutron (1.674 x 10^(-27) kg)





Characteristic Times of Different Objects

These are some of the characteristic times T of various objects:

Human

mass= 65 kg
T= 1.2e+36

Electron

mass= 9.11e-31 kg
T= 17276

Neutron

mass= 1.67492750e-27 kg
T= 31765072

Proton

mass= 1.67262192e-27 kg
T= 31721347

Earth

mass= 5.9e24 kg
T= 1.1e+59

Moon

mass= 7.3e22 kg
T= 1.4e+57

Sun

mass= 1.9e30 kg
3.7e+64

2.6 "Extra": Proving Constant Intensity in 3 Dimensions

Understanding Experimental Conditions:

$$\int_{\infty}^{\infty} P(x)dx = finite$$

$$P(x) \geq 0$$

For both of these to be true, $P(\infty) \to 0$ and $P(-\infty) \to 0$

$$\int_{\infty}^{\infty} dx \int_{\infty}^{\infty} dy \int_{\infty}^{\infty} dz P(x) = finite$$

We must simply use the same logic above and realize that the limit of P(x,y,z) as x/y/z approaches ∞ for all x,y; x,z; or y,z is 0.

Potential V(x,y,z)- not time-dependent Particle mechanics

$$\frac{P_x^2 + P_y^2 + P_z^2}{2m} + V(x,y,z) = E$$

Wave mechanics (same sorta idea)

$$\left[\frac{-\hbar^2}{2m}\left[\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right] + V(x,y,z)\right]\psi(x,y,z,t) = i\hbar\frac{d}{dt}\psi(x,y,z,t)$$

$$P(x,y,z,t) = \psi^*(x,y,z,t)\psi(x,y,z,t)$$

$$\psi^*\left[\frac{-\hbar^2}{2m}\left[\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} + V\right]\right]\psi = i\hbar\psi^*\frac{\partial}{\partial t}\psi$$

Take complex conjugate

$$\psi\left[\frac{-\hbar^2}{2m}\left[\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} + V\right]\right]\psi^* = -i\hbar\psi\frac{\partial}{\partial t}\psi^*$$

Subtract these two:

$$\frac{-\hbar^2}{2m}\left[\psi^*\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} + \cancel{V}\right)\psi - \psi\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} + \cancel{V}\right)\psi^*\right] = i\hbar\left[\psi\frac{d}{dt}\psi^* + \psi\frac{\partial}{\partial t}\psi^*\right]$$

$$\frac{\hbar^2}{2m}\left[\frac{\partial}{\partial x}\left(\psi\frac{\partial}{\partial x}\psi^* - \psi^*\frac{\partial}{\partial x}\psi\right) + \frac{\partial}{\partial y}\left(\psi\frac{\partial}{\partial y}\psi^* - \psi^*\frac{\partial}{\partial y}\psi\right) + \frac{\partial}{\partial z}\left(\psi\frac{\partial}{\partial z}\psi^* - \psi^*\frac{\partial}{\partial z}\psi\right)\right] = i\hbar\left[\psi\frac{\partial}{\partial t}\psi^* + \psi^*\frac{\partial}{\partial t}\psi\right]$$

$$\frac{\partial}{\partial x}\left(\psi\frac{\partial}{\partial x}\psi^* - \psi^*\frac{\partial}{\partial x}\psi\right) = \cancel{\frac{\partial\psi}{\partial x}\frac{\partial\psi^*}{\partial x}} + \psi\frac{\partial^2}{\partial x^2}\psi^* - \cancel{\frac{\partial\psi^*}{\partial x}\frac{\partial\psi}{\partial x}} - \psi^*\frac{\partial^2}{\partial x^2}\psi = \frac{\partial}{\partial x}\left(\psi\frac{\partial}{\partial x}\psi^* - \psi^*\frac{\partial}{\partial x}\psi\right)$$

We want to show that in 3 dimensions, the probability over all of space is a constant that does not change over time. The integral of the probability over all of space would be:

$$\int_{-\infty}^{\infty}dz\int_{-\infty}^{\infty}dy\int_{-\infty}^{\infty}dx\frac{\partial}{\partial x}\left(\psi\frac{\partial}{\partial x}\psi^* - \psi^*\frac{\partial}{\partial x}\psi\right) = \int_{-\infty}^{\infty}dz\int_{-\infty}^{\infty}dy\left[\psi\frac{\partial}{\partial x}\psi^* - \psi^*\frac{\partial}{\partial x}\psi\right]_{-\infty}^{\infty} = 0$$

Looking at the other side of the wave equation, and performing this same integral

$$\implies \int_{-\infty}^{\infty}dz\int_{-\infty}^{\infty}dy\int_{-\infty}^{\infty}dx\, i\hbar\left[\psi\frac{\partial}{\partial t}\psi^* + \psi^*\frac{\partial}{\partial t}\psi\right] = 0$$

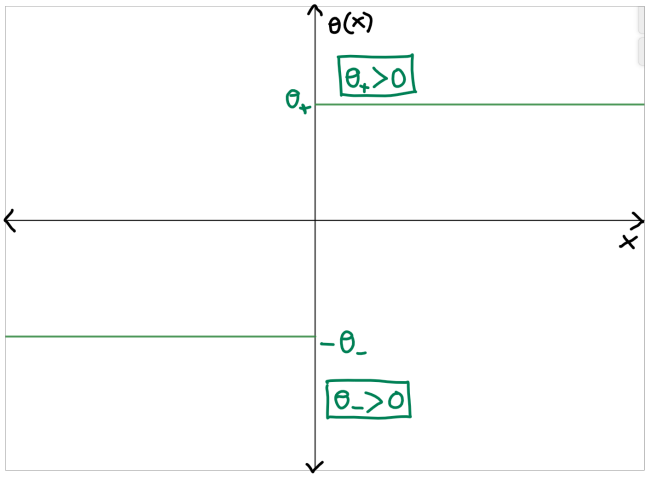
$$\implies i\hbar\int_{-\infty}^{\infty}dz\int_{-\infty}^{\infty}dy\int_{-\infty}^{\infty}dx\,\frac{\partial}{\partial t}\left(\psi\psi^*\right) = 0$$

$$\implies \frac{\partial}{\partial t}\left[\int_{-\infty}^{\infty}dz\int_{-\infty}^{\infty}dy\int_{-\infty}^{\infty}dx\,\left(\psi\psi^*\right)\right] = 0$$

Since $\psi\psi^* = P(x,y,z,t)$, this means the total probability/intensity is a constant. If we normalize the total intensity to 1, then it will be 1 always.

2.7 "Extra": Delta Dirac function as the result of the derivation of a step function

$$\int_{-\infty}^{\infty}f(x)\delta(x-y)dx = f(y)$$



For this graph, what is $\frac{d\theta}{dx}$?

$$Limit_{\epsilon\to\infty}\frac{\theta(x+\epsilon)-\theta(x-\epsilon)}{2\epsilon}=\infty$$

f(x) is some function that is continuous and we want to find:

$$\int_{-\infty}^{\infty} f(x)\frac{d\theta}{dx}dx=\int_{-\infty}^{\infty}\left[\frac{d}{dx}[f(x)\theta(x)]-\theta(x)\frac{df}{dx}\right]dx$$

$$=[f(x)\theta(x)]_{-\infty}^{\infty}-\int_{-\infty}^{\infty}\theta(x)\frac{df}{dx}dx$$

$$=f(\infty)\theta_+ + f(-\infty)\theta_- + \theta_-\int_{-\infty}^{0}\frac{df}{dx}dx-\theta_+\int_{0}^{\infty}\frac{df}{dx}dx$$

$$=f(\infty)\theta_+ + f(\infty)\theta_- + \theta_-[f(x)]_{-\infty}^{0}-\theta_+[f(x)]_{0}^{\infty}$$

$$=f(\infty)\theta_+ + f(\infty)\theta_- + \theta_-(f(0)-f(-\infty))-\theta_+(f(\infty)-f(0))$$

$$=\cancel{f(\infty)\theta_+}+\cancel{f(\infty)\theta_-}+\theta_-f(0)-\cancel{\theta_-f(-\infty)}-\cancel{\theta_+f(\infty)}+\theta_+f(0)$$

$$=f(0)[\theta_+ + \theta_-]$$

$$\therefore\frac{d\theta}{dx}=(\theta_+ + \theta_-)\delta(x)$$

Quantum Mechanics- Part 2

Melanie Frolich

October 2023

Contents

1 Potential Well

1.1 Adding a Potential

So far, we have examined only a free wave, which existed either on a certain length L or expanded through all of space and that had no potential energy through anywhere it existed. What types of simple models can we look at when adding a potential energy through a region of space. Well, let's start by rewriting our general wave equation into its time and position components.

$$\psi(x,t) = e^{i(kx-\omega t)} = \phi(x)e^{-i(\omega t)} = \phi(x)e^{-i\frac{E}{\hbar}t}$$

This new format makes it easier to plug this into the wave equation and ask the question, are there solutions to this?

Wave Equation:

$$i\bar{h}\frac{d\psi}{dt} = \frac{-\hbar^2}{2m}\frac{d^2\psi(x,t)}{dx^2} + V(x)\psi(x,t)$$

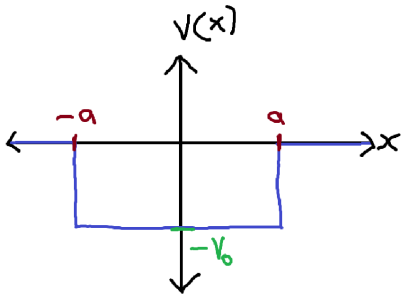
Plug in:

$$i\hbar\left(\frac{-iE}{\hbar}\right)\phi(x)e^{\frac{-iE}{\hbar}t} = \frac{-\hbar^2}{2m}\frac{d^2\phi}{dx^2}e^{\frac{-iE}{\hbar}t} + V(x)\phi(x)e^{\frac{-iE}{\hbar}t}$$

(Notice that the potential energy is independent of time, this is easier to solve for us).

If $V(x) = 0$, there is no solution (examine second derivative of $\phi(x)$)

Since the typical potential, $\frac{constant}{x^2}$ is hard to solve and we are merely undergraduate students doing our best, let's try a potential that looks like this:



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Briefly on Force

What happens if we look at the force of this potential, in other words the derivative of this potential with respect to position?

Well, it will be zero for most of the potential graph, but, at the "jumps" it will be equal to the property shown at the end of "Quantum Notes 1", in other words, at each jump this function will look like:

$$\frac{dV}{dx} @ -a = (\theta_+ + \theta_-)\delta(x) = (-V_0 - 0)\delta(-a)$$

$$\frac{dV}{dx} @ a = (\theta_+ + \theta_-)\delta(x) = (0 - (-V_0))\delta(a)$$

Often, the delta dirac function is interpreted as being infinite in one location, or at least a "big spike" so we can kind of imagine that at the edges of the potential the particle can be thought of as instantly "bouncing off" the edges and changing directions after having experienced a very large force.

.....

1.2 Classical Context

We know from classical mechanics that for a bound state, the total energy must be negative (if it is positive then there is enough kinetic energy to make the system no longer bound), meaning that:

$$E = \frac{1}{2}mv^2 - V_0 < 0$$

With this understanding, let's change the sign of E for simplicity in math and declare that:

$$TotalEnergy = -E$$

Meaning:

$$\therefore -E = \frac{1}{2}mv^2 - V_0 < 0 \implies V_0 - E = \frac{1}{2}mv^2$$

The value of E (which is now -(Total Energy)) has to be less than V_0. This makes sense intuitively because the total energy HAS to larger than the potential energy $(-V_0)$:

$$-E < -V_0 \implies E < V_0$$

But it can also be shown mathematically because if E is not smaller than V_0, you would get an imaginary value for velocity. :

$$v = \sqrt{\frac{2(V_0 - E)}{m}} \therefore E < V_0$$

OK, let's change our signs for everything else we've already established. The wave function and wave equation become:

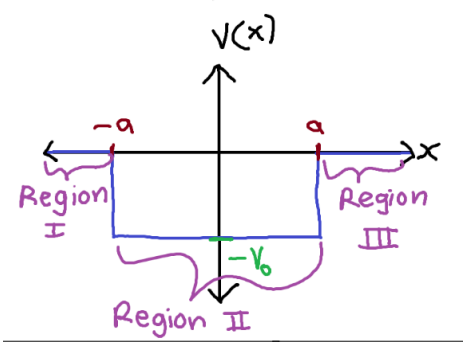
$$\psi(x,t) = \phi(x)e^{\frac{iE}{\hbar}t}$$

$$i\hbar\frac{iE}{\hbar}\phi(x)\cancel{e^{\frac{iE}{\hbar}t}} = \frac{-\hbar}{2m}\frac{d^2\phi}{dx^2}\cancel{e^{\frac{iE}{\hbar}t}} + V(x)\phi(x)\cancel{e^{\frac{iE}{\hbar}t}}$$

$$\implies -E\phi(x) = \frac{-\hbar}{2m}\frac{d^2\phi}{dx^2} + V(x)\phi(x)$$

$$\implies \frac{\hbar}{2m}\frac{d^2\phi}{dx^2} = (E + V(x))\phi(x)$$

$$\implies \frac{d^2\phi}{dx^2} = \frac{2m}{\hbar^2}(E + V(x))\phi(x)$$



Looking at the three regions of this graph we have:

Region I

$$\frac{d^2\phi}{dx^2} = \frac{2mE}{\hbar^2}\phi(x)$$

where $\frac{2mE}{\hbar^2} > 0$

Region II

$$\frac{d^2\phi}{dx^2} = -\frac{2mE}{\hbar^2}(V_0 - E)\phi(x)$$

where $\frac{2mE}{\hbar^2} > 0$

Region III

$$\frac{d^2\phi}{dx^2} = \frac{2mE}{\hbar^2}\phi(x)$$

where $\frac{2mE}{\hbar^2} > 0$

Since we know that any measurements taken as intensities or as probabilities of a particle being found at a certain location ($P(x) = \phi^2(x)$) must all be positive and finite and can be normalized so that the following condition is true:

$$\int_{-\infty}^{\infty} \phi^2(x)dx = 1$$

Then, we know that this condition implies that for any $\phi(x)$:

$$\phi(-\infty) = 0$$

$$\phi(\infty) = 0$$

This detail will help in finding energy value for a given finite potential well and ultimately solving this problem.

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Introducing α and finding better units for this problem

For regions I and III, What is this?:

$$\frac{2mE}{\hbar^2}$$

We'll look at the units to try to understand.

$$\frac{2mE}{\hbar^2} : \frac{kgJ}{(Js)^2} = \frac{1}{m^2}$$

We want to have a better understanding of the general forms that these square well problems take on through values that do not rely on the mass of the particle or the width of the well. So we will convert to "natural units" by multiplying by the width of the well:

$$\alpha = a\sqrt{\frac{2mE}{\hbar^2}}$$

This α is a way of defining the energy so that we can find the trend of energy distributions for a set of square well potentials. As such, it is clearer to see that they are same, but simply scaled differently by various factors, namely the width, mass, and total energy in SI units.

For region II we do something similar but we change the sign of the region:

$$\beta = a\sqrt{\frac{2m(V_0 - E)}{\hbar^2}}$$

Both α and β are constants dependent on the potential well width, total energy, and in the case of beta, the potential well depth as well. In addition, the square of each of them must be a positive value. We can add these squares together to denote a new value, γ, which is dependent on only the potential well depth and potential well width.

$$\gamma^2 = \alpha^2 + \beta^2 = \frac{2mV_0a^2}{\hbar^2}$$

This γ in essence represents a set of all the possible, different combined solutions of α and β for a given combination of well depth, mass, and width. When comparing it to the other terms in this equation, α and β, it is notable that γ is dependent on V_0 and not E, so it can be thought of as representing the well depth. It is not dependent on the total energy and thus may represent solutions for various total energies (α values) of a given well.

γ and Natural Units

When setting up a particular square well potential model, the relevant information determining the state of the model includes the depth of the square well potential, its width, and the mass of the particle or object of the model. These values are all included in γ which is in essence an identifying value for a given problem.

In addition, γ can be thought of as the potential in the given "natural units" of the model. Let's elaborate on this. γ^2 is as follows:

$$\alpha^2 + \beta^2 = \gamma^2 = \frac{a^2mV_0}{\hbar^2} = \frac{V_0}{(\frac{\hbar^2}{2ma^2})}$$

Now we've rearranged γ as some potential well depth value divided by a particular denominator which is dependent on the width of the well (a) and the mass of the particle m. Let's examine the units of this denominator more closely:

$$\frac{\hbar^2}{2ma^2}\ units = \frac{J^2\ sec^2}{kg\ m^2} = \frac{J^2}{\frac{kg\ m^2}{sec^2}} = J$$

Therefore this is a particular value in Joules for the given problem, and we are dividing the well potential by it. γ is basically measuring the well depth (V_0) in a unit created by the model itself. It is measuring the well depth in the "natural units" of the problem.

.....

We can rewrite our equations for each region from before using this new notation:

Region I

$$\frac{d^2\phi}{dx^2} = \frac{\alpha^2}{a^2}\phi(x)$$

where $\alpha^2 > 0$

Region II

$$\frac{d^2\phi}{dx^2} = \frac{-\beta^2}{a^2}\phi(x)$$

where $\beta^2 > 0$

Region III

$$\frac{d^2\phi}{dx^2} = \frac{\alpha^2}{a^2}\phi(x)$$

where $\alpha^2 > 0$

When thinking of how to solve this problem, it might simply feel instinctual that $\phi(x)$ should be continuous. But instinctual is insufficient proof, so let's examine the wave equation (when $-E = (total\ energy)$) to understand where this assertion arises from:

$$-E\phi(x) = \frac{-\hbar}{2m}\frac{d^2\phi}{dx^2} + V(x)\phi(x)$$

By looking at this, it seems that at most, $\frac{d^2\phi}{dx^2}$ can be discontinuous at $x = \pm a$ because at this location, the potential's "discontinuousness" when added to $V(x)$'s "discontinuousness" may cancel each other out and thus it would make sense that they could be equal to $-E\phi(x)$. But this would only happen at a and -a.

Also, $\frac{d^2\phi}{dx^2}$ cannot be a Dirac delta function (δ, the derivative of a step in a discontinuous function) because then it would not be possible to make the other side of the equation also a Dirac delta function. This means that if $\frac{d\phi}{dx}$ is discontinuous at some point $x = x_0$, then the derivative here ($\frac{d^2\phi}{dx^2}$) will be $\delta(x - x_0)$. We already established that $\frac{d^2\phi}{dx^2}$ cannot be a delta Dirac function so $\frac{d\phi}{dx}$ must be continuous everywhere.

Some educated guesses for each segment.:

$$x < -a: \qquad \phi(x) = De^{\frac{\alpha}{a}x} + 0e^{\frac{-\alpha}{a}x} = De^{\frac{\alpha}{a}x}$$

$$-a < x < a: \qquad \phi(x) = (Bsin(\frac{\beta}{a}x) + Ccos(\frac{\beta}{a}x))e^{-\alpha}$$

$$x > a: \qquad \phi(x) = 0e^{\frac{\alpha}{a}x} + Ae^{\frac{-\alpha}{a}x} = Ae^{\frac{-\alpha}{a}x}$$

For $x < -a$ and $x > a$ the reason the wave function must exponentially increase and exponentially decay respectively is in order to fulfill the condition $\int_{-\infty}^{\infty} \phi^2(x)dx = finite$

And, the reason the $-a < x < a$ section is multiplied by the factor $e^{-\alpha}$ is because it makes the math simpler.

In order to find solutions to this problem (which now consists of finding acceptable values for α and β) we will apply the previously discussed continuity conditions for $\phi(x)$ and $\frac{d\phi}{dx}$

$$\phi(x): \qquad \frac{d\phi}{dx}:$$

$$x=-a: \quad De^{-\alpha} = (-Bsin(\beta)+Ccos(\beta))e^{-\alpha} \quad D\frac{\alpha}{\phi}e^{-\alpha} = \left(B\frac{\beta}{\phi}cos\beta + C\frac{\beta}{\phi}sin\beta\right)e^{-\alpha}$$

$$x=a: \quad Ae^{-\alpha} = (Bsin(\frac{\beta}{a}x)+Ccos(\frac{\beta}{a}x))e^{-\alpha} \quad -A\frac{\alpha}{\phi}e^{-\alpha} = \left(B\frac{\beta}{\phi}cos\beta - C\frac{\beta}{\phi}sin\beta\right)e^{-\alpha}$$

Solving this system:

$$\alpha(A+D) = 2\alpha Ccos\beta = 2C\beta sin\beta$$
$$\implies C(\alpha cos\beta - \beta sin\beta) = 0$$

$$\therefore either\ C=0\ or\ \alpha cos\beta = \beta sin\beta$$

$$\alpha(A-D) = 2\alpha Bsin\beta = -2B\beta cos\beta$$
$$\implies B(\alpha sin\beta + \beta cos\beta) = 0$$

$$\therefore either\ B=0\ or\ \alpha sin\beta = -\beta cos\beta$$

3 potential solutions (B=0 and C=0 is a trivial solution because then there is no wave function)

1): $\alpha = \beta tan\beta$ and $B=0$

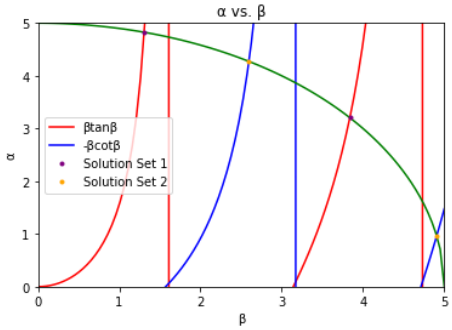
2): $C=0$ and $\alpha = -\beta cot\beta$

~~3)~~: $\alpha cos\beta = \beta sin\beta$ and $\alpha sin\beta = -\beta cos\beta$

$\implies \alpha sin^2\beta + \alpha cos^2\beta = 0 \implies \alpha = 0$

However, this solution 3 is not allowed based on the definition of alpha, where it is clear that $\alpha > 0$. (This is because α^2 is -(Total Energy) when α and Total Energy are in natural units. Therefore, since the total energy is negative in an attractive potential, α must be positive)

To find final values for α and β we must take into account both their definition with respect to γ and these above solutions. A graphical representation of possible values for β (and thus α based on the γ value of your particular setup) is shown below for a value of $\gamma = 5$



In addition, looking back at the continuity conditions we had established, these solutions tell us more information about the coefficients:

1): $B = 0$, $A = D = Ccos\beta$, and $\alpha = \beta tan\beta$

2): $C = 0$, $A = -D = Bsin\beta$, and $\alpha = -\beta cot\beta$

However, we still have not solved the wave function equation because we have not found all the values of the coefficients in terms of the intrinsic properties of the well and situation (γ). We are missing one coefficient (C in solution 1 and B in solution 2 are missing) and through the process of finding this, quantization will result.

1.3 Quantization

We are learning quantum mechanics, where does the quantization come in? In the case of the potential well, it arises due to both the intrinsic continuity conditions as well as at the time of normalization:

The requirement that $\int_{-\infty}^{\infty} \phi^2(x)dx = 1$ means that $\phi(x)$ must approach zero at its "ends" so as to end up with a finite number for the integral. In other words $\phi(\pm\infty) = 0$.

Solution Set 1 (Wave Function is Even)

So let's re-examine our solution 1) and rewrite $\phi(x)$ in terms of these values: $B = 0$, $A = D = Ccos\beta$, and $\alpha = \beta tan\beta$:

$$x < -a: \qquad \phi(x) = De^{\frac{\alpha}{a}x} = Ccos\beta e^{\frac{\alpha}{a}x}$$

$$-a < x < a: \qquad \phi(x) = Ccos(\frac{\beta}{a}x))e^{-\alpha}$$

$$x > a: \qquad \phi(x) = Ae^{\frac{-\alpha}{a}x} = Ccos\beta e^{\frac{-\alpha}{a}x}$$

Now, based on this wave function let's perform the integral $\int_{-\infty}^{\infty} \phi^2(x)dx = 1$:

$$\int_{-\infty}^{\infty} \phi^2(x)dx = C^2\left[\left(cos^2\beta\int_{-\infty}^{-a} e^{2\frac{\alpha}{a}x}dx\right) + \left(e^{-2\alpha}\int_{-a}^{a} cos^2(\frac{\beta}{a}x)dx\right) + \left(cos^2\beta\int_{a}^{\infty} e^{-2\frac{\alpha}{a}x}dx\right)\right]$$

Remember $cos^2(\frac{\beta}{a}x) = \frac{cos(\frac{2\beta}{a}x)+1}{2}$

$$= C^2[cos^2\beta\frac{a}{2\alpha}e^{\frac{2\alpha x}{a}}|_{-\infty}^{a} + \frac{e^{-2\alpha}}{2}\frac{a}{2\beta}(sin^2(\frac{\beta}{a}x) + x)|_{-a}^{a} - cos^2\beta\frac{a}{2\alpha}e^{\frac{-2}{a}}|_{a}^{\infty}]$$

$$\frac{C^2}{2}[\frac{2a}{\alpha}cos^2\beta e^{-2\alpha} + e^{-2\alpha}(\frac{a}{\beta}sin(2\beta) + 2a)]$$

$$= C^2ae^{-2\alpha}[\frac{1}{\alpha}cos^2\beta + \frac{sin2\beta}{2\beta} + 1]$$

Remember for this solution $\alpha = \beta tan\beta = \beta\frac{sin\beta}{cos\beta}$

$$= C^2 a e^{-2\alpha}[\frac{cos^3\beta}{\beta sin\beta} + \frac{sin\beta cos\beta}{\beta} + 1]$$

$$= C^2 a e^{-2\alpha}[\frac{cos\beta}{\beta sin\beta}(cos^2\beta + sin^2\beta) + 1]$$

$$= C^2 a e^{-2\alpha}[\frac{1}{\beta tan\beta} + 1] = C^2 a e^{-2\alpha}[\frac{1}{\alpha} + 1] = 1$$

$$\implies C^2 = \frac{\alpha e^{2\alpha}}{a(1+\alpha)}$$

Therefore:

$$x < -a: \qquad \phi(x) = \sqrt{\frac{\alpha e^{2\alpha}}{a(1+\alpha)}} cos\beta e^{\frac{\alpha}{a}x}$$

$$-a < x < a: \qquad \phi(x) = \sqrt{\frac{\alpha e^{2\alpha}}{a(1+\alpha)}} cos(\frac{\beta}{a}x)) e^{-\alpha}$$

$$x > a: \qquad \phi(x) = \sqrt{\frac{\alpha e^{2\alpha}}{a(1+\alpha)}} cos\beta e^{\frac{-\alpha}{a}x}$$

Finally, if we want to change the units of position x to natural units, we would divide by the well width a, so $y = \frac{x}{a}$ and we can create a new wave function in these units:

$$y < -1: \qquad \phi(y) = \sqrt{\frac{\alpha e^{2\alpha}}{(1+\alpha)}} cos\beta e^{\alpha y}$$

$$-1 < y < 1: \qquad \phi(x) = \sqrt{\frac{\alpha e^{2\alpha}}{(1+\alpha)}} cos(\beta y)) e^{-\alpha}$$

$$y > 1: \qquad \phi(x) = \sqrt{\frac{\alpha e^{2\alpha}}{(1+\alpha)}} cos\beta e^{-\alpha y}$$

Solution Set 2 (Wave Function is Odd)

This same normalization can be performed for solution 2 (where C=0, A=-D=Bsinβ) to find the following values for wave function and coefficient B:

$$x < -a: \qquad \phi(x) = -Bsin\beta e^{\frac{\alpha}{a}x}$$

$$-a < x < a: \qquad \phi(x) = Bsin(\frac{\beta}{a}x) e^{-\alpha}$$

$$x > a: \qquad \phi(x) = Bsin\beta e^{\frac{-\alpha}{a}x}$$

$$B^2 = \frac{\alpha e^{2\alpha}}{a(1+\alpha)}$$

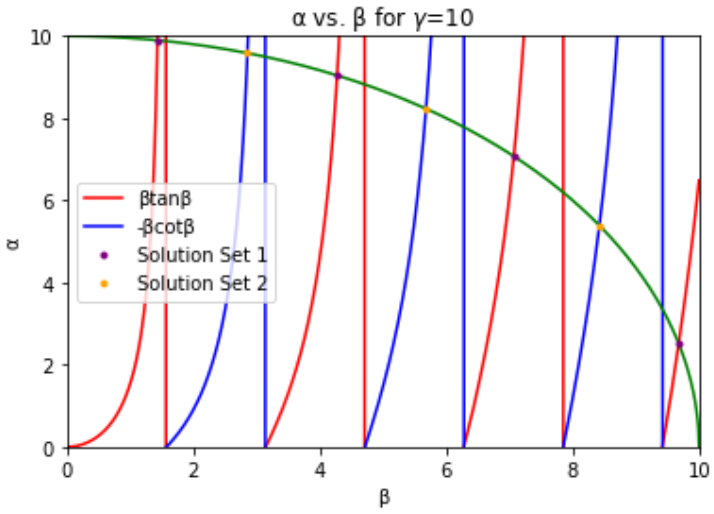
Once more substituting this new value for B and in natural units of length we get:

$$y < -1: \qquad \phi(y) = -\sqrt{\frac{\alpha e^{2\alpha}}{(1+\alpha)}} sin\beta e^{\alpha y}$$

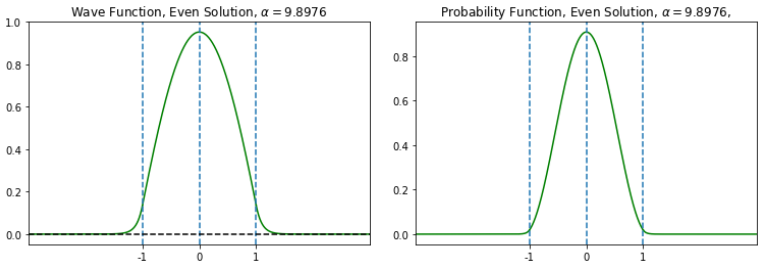
$$-1 < y < 1: \qquad \phi(x) = \sqrt{\frac{\alpha e^{2\alpha}}{(1+\alpha)}} sin(\beta y) e^{-\alpha}$$

$$x > 1: \qquad \phi(x) = \sqrt{\frac{\alpha e^{2\alpha}}{(1+\alpha)}} sin\beta e^{-\alpha y}$$

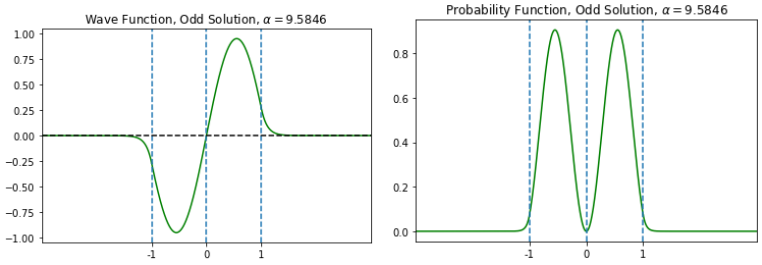
1.4 Example: γ=10



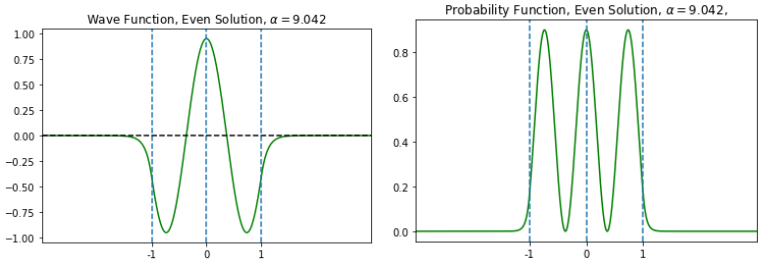
Below are the wave functions and probability functions for $\gamma = 10$. Solution Set 1 consists of all even wave functions below and Solution Set 2 consists of all the odd wave functions. The graphs are ordered from lowest energy to highest and are in natural units, where the edges of the potential well are at y=-1 and y=1



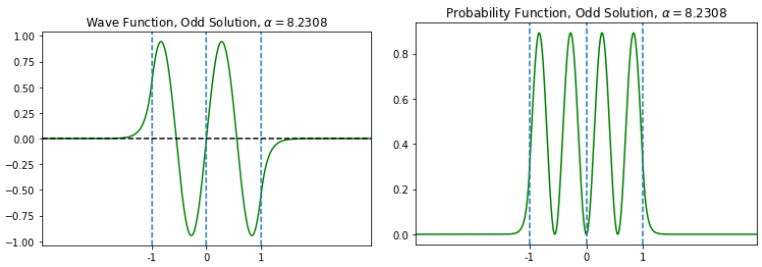
Energy in natural units: -97.96
Probability of finding the particle outside of the well: 0.002



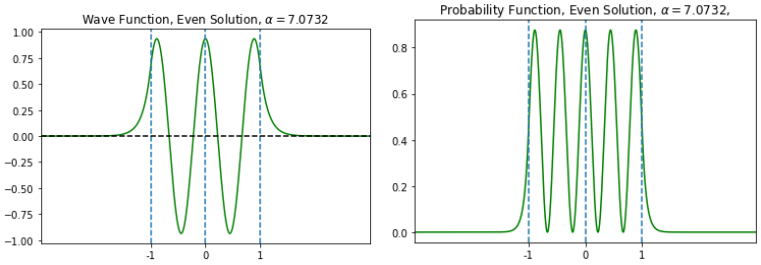
Energy in natural units: -91.86
Probability of finding the particle outside of the well: 0.008



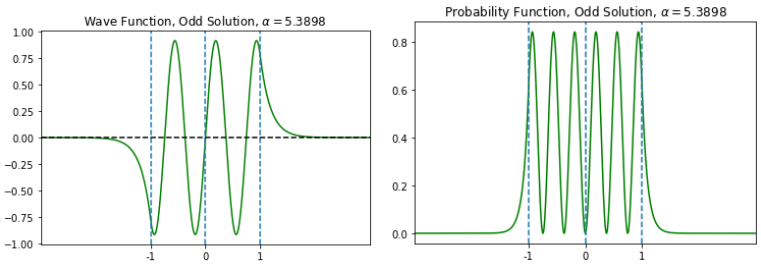
Energy in natural units: -81.76
Probability of finding the particle outside of the well: 0.018



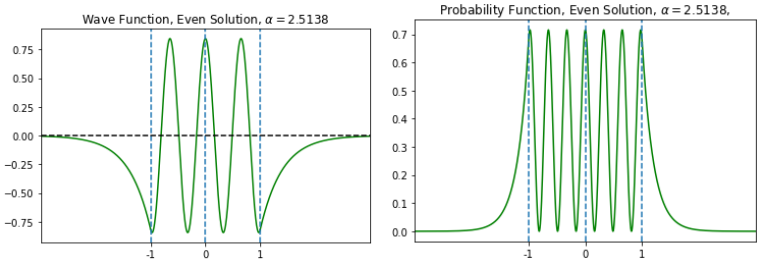
Energy in natural units: -67.75
Probability of finding the particle outside of the well: 0.035



Energy in natural units: -50.03
Probability of finding the particle outside of the well: 0.062

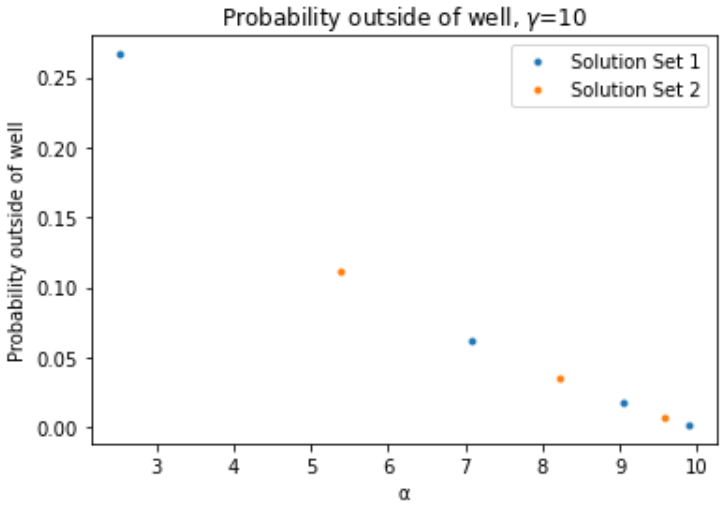


Energy in natural units: -29.05
Probability of finding the particle outside of the well: 0.111

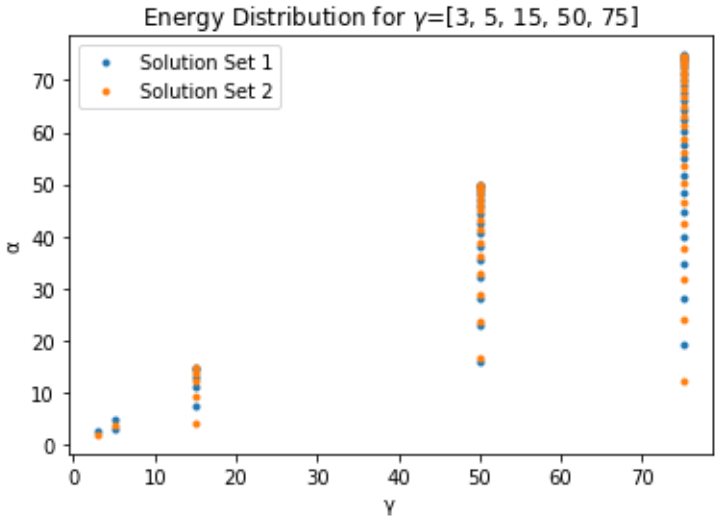


Energy in natural units: -6.32
Probability of finding the particle outside of the well: 0.267

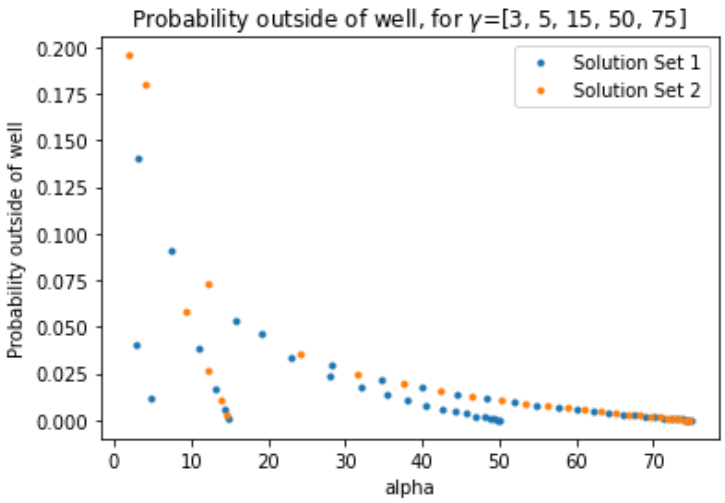
The graph below shows the probability of the particle or mass existing outside of the potential well, which classically would be 0 for a bound state since there would not be enough energy to overcome the potential energy barrier. However, this is no longer the case for this quantum mechanical model, and as it turns out, for a given γ value there is a higher probability for the lower α (higher energy) particles to exist outside the well



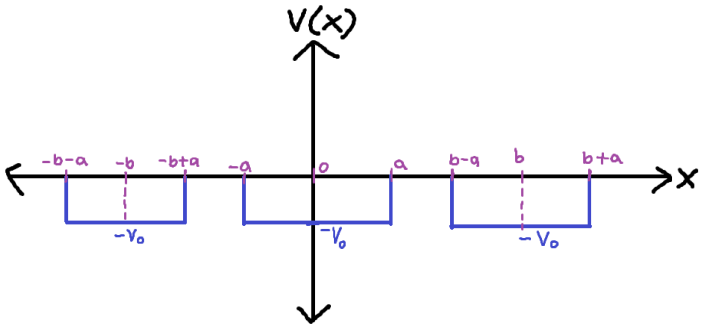
There is a lower possible energy as the value of γ increases as shown in the graph below. This makes sense in relation to the total energy constrictions wherein the total energy cannot be less than the potential well. For a deeper or more significant potential well, it would make sense that the lowest total energy could be a lower value.



Below is a graph showing the probability of a particle existing outside of the potential well for multiple different well depths.



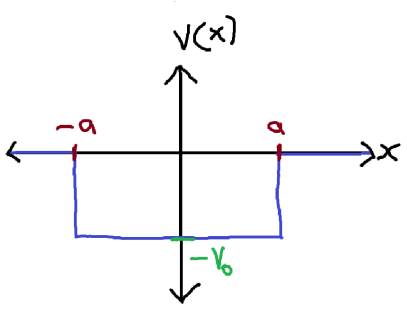
2 Building to Multiple Attractive Centers/Wells



This 1-dimensional model with multiple attractive wells, often called the Kronig-Penney model, starts to build a basic understanding of conductors and insulators and why they work like they do. Our goal is to work towards understanding of this model step by step.

How do you find the changes in energy for a model like this one? We're going to start by expanding on our understanding of a single attractive center and working with it as a delta function confined to a single region in space as opposed to a square well.

2.1 Understanding One Attractive Center



Due to dealing with an attractive potential in a bound state, every solution has to satisfy (where Total Energy is $-E$ and the potential depth is $-V_0$):

$$0 < E < V_0$$

The area of each square well is $2V_0a$, meaning:

$$\int_{-a}^{a} V(x)dx = -2C$$

where $C = V_0a$

This means that, in a sense:

$$"V(x) = -2C\delta(x)"$$

We can conceptualize this as taking the potential well and compressing its entire area to a single point, x=0. The depth would become infinitely deep and the width would become infinitely narrow.

Plugging this into the wave equation:

$$"\frac{-\hbar^2}{2m}\frac{d^2\phi}{dx^2} - 2c\delta(x)\phi(x) = -E\phi(x)"$$

(where remember $-E = \ Energy$ and $\phi(x,t) = e^{\frac{iE}{\hbar}t}\phi(x)$

Rewriting this:

$$\implies \frac{d^2\phi}{dx^2} + \frac{4mc}{\hbar^2}\delta(x)\phi(x) = \frac{2mE}{\hbar}\phi(x)$$

$$\implies \frac{d^2\phi}{dx^2} + \frac{4mV_0a}{\hbar^2}\delta(x)\phi(x) = \frac{2mE}{\hbar}\phi(x)$$

$$\implies \frac{d^2\phi}{dx^2} + 2g\delta(x)\phi(x) = \alpha^2\phi(x)$$

where $g = \frac{2mV_0a}{\hbar^2} > 0$ and $\alpha^2 = \frac{2mE}{\hbar} > 0$

So, based on this, is ϕ continuous as x=0?

Well, if ϕ is discontinuous at x=0, then $\frac{d\phi}{dx}|_{x=0}$ has to be $\delta(x)$ and $\frac{d^2\phi}{dx^2}|_{x=0}$ will be "worse" (even harder to define) than $\delta(x)$. Therefore, ϕ has to be continuous at x=0.

Is $\frac{d\phi}{dx}$ continuous at x=0?

No, and the jump must "match" $\delta(x)$ in the potential term!

What about away from x=0?

Away from x=0, the wave equation simplifies to the following (because $V(0 < x < 0) = 0$):

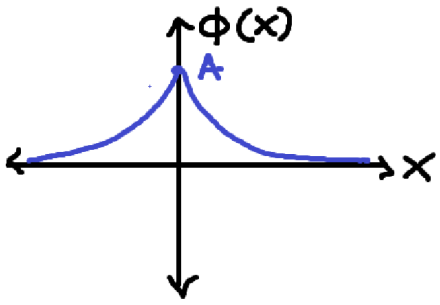
$$\frac{d^2\phi}{dx^2} = \alpha^2\phi$$

Therefore the wave function will look as follows (taking into account the need to normalize the probability function)

$$x \leq 0 : \qquad \phi(x) = Ae^{\alpha x}$$

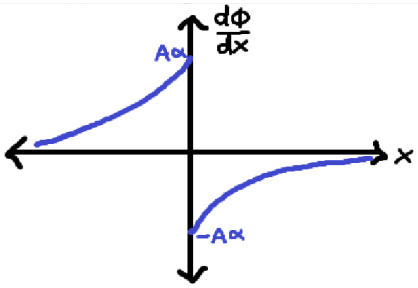
$$x \geq 0 : \qquad \phi(x) = Ae^{-\alpha x}$$

Therefore at $x = 0$, $\phi(x) = A$



$$x < 0 : \qquad \frac{d\phi(x)}{dx} = A\alpha e^{\alpha x}$$

$$x > 0 : \qquad \frac{d\phi(x)}{dx} = -A\alpha e^{-\alpha x}$$

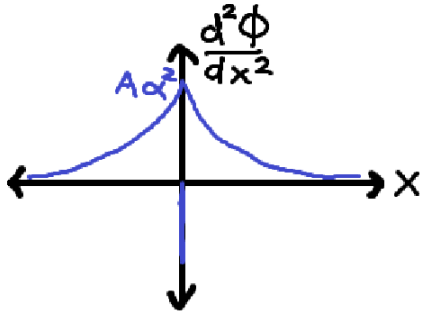


$$x < 0 : \qquad \frac{d^2\phi(x)}{dx^2} = A\alpha^2 e^{\alpha x}$$

$$x > 0 : \qquad \frac{d^2\phi(x)}{dx^2} = A\alpha^2 e^{-\alpha x}$$

$$+B\delta(x)$$

Since $\frac{d\phi}{dx}$ jumps from positive to negative, $B < 0$.



$$\int_{-\infty}^{\infty} \frac{d^2\phi}{dx^2} dx = \frac{d\phi}{dx}|_{x=0} - \frac{d\phi}{dx}|_{x=-\infty}$$

$$A\alpha^2 \int_{-\infty}^{0} e^{\alpha x} dx + A\alpha^2 \int_{0}^{\infty} e^{-\alpha x} dx + B \int_{-\infty}^{\infty} \delta(x) dx = -A\alpha e^{-\alpha x}|_{x=\infty}$$

$$\implies 2A\alpha + B = 0 \implies B = -2A\alpha$$

Now, back to examining at x=0:

$$"\alpha^2\phi(x) = \frac{d^2\phi}{dx^2} + 2g\delta(x)\phi(x)"$$

Integrate this:

$$\alpha^2 A \int_{-\infty}^{0} e^{\alpha x} dx + \alpha^2 A \int_{0}^{\infty} e^{-\alpha x} dx = \int_{-\infty}^{\infty} \frac{d^2\phi}{dx^2} dx + 2g \int_{-\infty}^{\infty} \delta(x)\phi(x) dx$$

$$\implies \alpha A e^{\alpha x}|_{-\infty}^{0} - \alpha A e^{-\alpha x}|_{0}^{\infty} = 0 + 2g\phi(0)$$

$$\implies 2\alpha A = 2gA$$

$$\implies \alpha = g$$

We can thus write the probability function as:

$$x \leq 0 : \qquad P(x) = A^2 e^{2gx}$$
$$x \geq 0 : \qquad P(x) = A^2 e^{-2gx}$$

And we can use to the fact that $\int_{-\infty}^{\infty} P(x)dx = 1$ to find solve for A^2:

$$\frac{2A^2}{2g} = 1$$

$$\implies A^2 = g$$

Therefore we can rewrite the $\phi(x)$ solution as:

$$x \leq 0 : \qquad \phi(x) = \sqrt{g}e^{gx}$$
$$x \geq 0 : \qquad \phi(x) = \sqrt{g}e^{-gx}$$

Remember that g is related to the potential of the well:

$$g = \frac{2mV_0 a}{\hbar^2}$$

And the bigger the g the more "localized" the solution. This makes sense because you are saying that the stronger the potential, the more likely that the wave function is found there.

Summary of what we just did:
1) $\phi(x)$ for $x > 0$ and $x < 0$
2) Make $\phi(x)$ continuous at x=0 (because it has to be)
3) $\frac{d\phi}{dx}|_{x=0^-} - \frac{d\phi}{dx}|_{x=0^+} = 2g\phi(0)$

2.2 Multiple Wells (work in progress)

Let's imagine we have N number of attractive centers located at $x = d, 2d, ..., nd$, and at each of them there is a dirac delta function $\delta(x)$.

We set $g = \frac{2mV_0 a}{\hbar^2} = 1$ and furthermore understand the potential energy to be the following:

$$V(x) = -2V_0 a \left[\sum_{n=1}^{N} \delta(x - nd)\right]$$

Much like before, we know that away from the attractive centers the wave equation simplifies to:

$$\frac{d^2\phi}{dx^2} = \alpha^2 \phi$$

And at the attractive centers:

$$"\alpha^2\phi(x) = \frac{d\phi^2}{dx^2} + 2\left[\sum_{n=1}^{N} \delta(x - nd)\right]\phi(x)"$$

We know that since $\phi(x)$ must be continuous at this delta function location ($x = nd$)we can create the condition:

$$A_{n-1}e^{-\alpha\frac{d}{2}} + B_{n-1}e^{\alpha\frac{d}{2}} = A_n e^{\alpha\frac{d}{2}} + B_n e^{-\alpha\frac{d}{2}}$$

We can rewrite this in a nicer way by defining $v = e^{-\alpha\frac{d}{2}}$:

$$I) \qquad A_{n-1}v + B_{n-1}\frac{1}{v} = A_n\frac{1}{v} + B_n v$$

In addition, much like before we know that since there is a dirac delta function we know:

$$\frac{d\phi}{dx}|_{x=nd^-} - \frac{d\phi}{dx}|_{x=nd^+} = 2\phi(nd)$$

Rewritten this becomes:

$$[-\alpha A_{n-1}v + \alpha B_{n-1}\frac{1}{v}] - [-\alpha A_n\frac{1}{v} + \alpha B_n v] = 2A_{n-1}v + 2B_{n-1}\frac{1}{1}$$

$$\implies A_{n-1}(-\alpha v - 2v) + B_{n-1}(\frac{\alpha}{v} - \frac{2}{v}) = -\alpha A_n\frac{1}{v} + \alpha B_n v$$

$$\implies \quad II) \qquad -vA_{n-1}(1+\tfrac{2}{\alpha}) + \tfrac{1}{v}B_{n-1}(1-\tfrac{2}{\alpha}) = -A_n\tfrac{1}{v} + B_n v$$

Adding I) and II):

$$\cancel{2}B_n v = \frac{-\cancel{2}v}{\alpha}A_{n-1} + (\frac{\cancel{2}}{v} - \frac{\cancel{2}}{\alpha v})B_{n-1}$$

Subtracting I) and II):

$$\cancel{2}A_n\frac{1}{v} = (\cancel{2}\pi + \frac{\cancel{2}v}{\alpha})A_{n-1} + \frac{\cancel{2}}{\alpha v}B_{n-1}$$

Therefore:

$$B_n = \frac{-1}{\alpha}A_{n-1} + \frac{1}{v^2}(1-\frac{1}{\alpha})B_{n-1}$$

$$A_n = v^2(1+\frac{1}{\alpha})A_{n-1} + \frac{1}{\alpha}B_{n-1}$$

Or, written in matrix format:

$$\begin{pmatrix} A_n \\ B_n \end{pmatrix} = \begin{pmatrix} v^2(1+\frac{1}{\alpha}) & \frac{1}{\alpha} \\ \frac{-1}{\alpha} & \frac{1}{v^2}(1-\frac{1}{\alpha}) \end{pmatrix} \begin{pmatrix} A_{n-1} \\ B_{n-1} \end{pmatrix}$$

We will name this transformation matrix from A_{n-1} and B_{n-1} to A_n and B_n as $T(\alpha, d)$. Note that this matrix has no dependence on which of the N attractive centers we are transforming to or from. This means that we can imagine that for each attractive center there exists this same transformation matrix that transforms from one side of it to the other, like so:

And thus for the total scenario of N attractive centers we end up with:

$$\begin{pmatrix} A_N \\ B_N \end{pmatrix} = T^N \begin{pmatrix} A_0 \\ B_0 \end{pmatrix}$$

However, looking at the image we know that at the ends of the wave function, as it approaches ∞ and $-\infty$ the function must approach 0. This means that this matrix simplifies to:

$$\begin{pmatrix} A_N \\ 0 \end{pmatrix} = \begin{pmatrix} (T^N)_{11} & (T^N)_{12} \\ (T^N)_{21} & (T^N)_{22} \end{pmatrix} \begin{pmatrix} 0 \\ B_0 \end{pmatrix}$$

Yielding the two equations:

$$A_n = (T^N)_{12} B_0$$

$$0 = (T^N)_{22} B_0$$

We know that $B_0 \neq 0$ for the wave function to actually exist so $(T^N)_{22} = 0$.

2.3 Putting Them On a Circle

So far, we have been imagining our wells on an infinite flat line. However, there are benefits to instead modeling these potential wells as existing on a circle. Much like a periodic function repeats while as you move down it, a circle repeats intrinsically due to its shape:

For this new geometry, we can now state that:

$$V(x + L) = V(x)$$
$$V(x + d) = V(x)$$
$$Nd = L$$

Previously, for our flat line we had the restriction that $\int_0^L \psi^2(x)dx = 1$. We extending this flat line L out towards infinity, meaning $\int_{-\infty}^{\infty} \psi^2(x)dx = 1$ which further has the consequence that the ends of our wave function must go towards zero ($\psi(-\infty) = \psi(\infty) = 0$).

However, with the circle, we no longer have this restriction on the ends, yet, when making the length L go to ∞, this circle turns into a flat line at any point anyways.

Now, with the circle, this restriction on the ends of the wave function no longer applies.

.....

Definition of "Bound"

Before, we had one or multiple attractive potentials, and said the wave function was "bound" thus it didn't exist at the edges (approaching $-\infty$ and ∞). Now, with this model on a circle, "bound" refers simply to attractive centers existing.

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Going back to the modified wave equation we used previously but this time looking for solutions of the type $\psi(x,t) = e^{\frac{-iE}{\hbar}t}\phi(x)$ (Notice we are no longer changing the sign of E as we did previously):

$$-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\phi(x) - V(x)\phi(x) = -E\phi(x)$$
$$\implies -\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\phi(x) = V(x)\phi(x) - E\phi(x)$$

Where Energy = E and E¿0

Our periodic boundary conditions are now:

$$\phi(x) = \phi(x+L)$$
$$\frac{d\phi}{dx}(x) = \frac{d\phi}{dx}(x+L)$$
$$V(x) = V(x+L)$$

Given the first condition, plugging x into the left hand side of the above wave equation should give the same result as plugging in x+L, meaning:

$$\frac{d^2\phi}{dx^2}(x) = \frac{d^2\phi}{dx^2}(x+L)$$

In addition to these periodic boundary conditions for this circle, we have a set of conditions for the particular problem type we want to solve:

$$V(x) = V(x+d)$$

$$Nd = L$$

This all begs the question of whether $\phi(x) = \phi(x+d)$?

Comparing:

$$-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\phi(x) = V(x)\phi(x) - E\phi(x)$$

And:

$$-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\phi(x+d) = V(x+d)\phi(x+d) - E\phi(x+d) = V(x)\phi(x+d) - E\phi(x+d)$$

It is apparent that $\phi(x+d) = \phi(x)$

$$\therefore \phi(x+2d) = C\phi(x+d) = C^2\phi(x)$$
$$\phi(x+kd) = C^k\phi(x)$$
$$\phi(x+Nd) = C^N\phi(x) = \phi(x)$$

$$\implies C^N = 1 = e^{i2\pi k}$$
$$\implies C = e^{\frac{i2\pi}{N}k}$$

Where k=0,1,2,..,N-1

Therefore, for $\phi(x+Nd)$ when N=1,

$$\phi(x+d) = C\phi(x) = e^{\frac{i2\pi k}{N}}\phi(x)$$
$$\frac{d\phi(x+d)}{dx} = e^{\frac{i2\pi k}{N}}\frac{d\phi(x)}{dx}$$

For this delta function potential centered at x=0, we define once more the wave equation:

$$\frac{d^2\phi}{dx^2} - \frac{2m}{\hbar^2}V(x)\phi(x) = \frac{-2mE}{\hbar^2}\phi(x)$$

We can define two values for total energy in natural units depending on whether the energy is negative or positive:

$$E < 0: \qquad \alpha^2$$
$$E > 0: \qquad -\beta^2$$

If $x \neq 0$:

$$E < 0: \qquad \frac{d\phi}{dx} = \alpha^2\phi$$
$$E > 0: \qquad \frac{d\phi}{dx} = -\beta^2\phi$$

And at $x = 0$ we have the following δ-function condition:

$$\frac{d\phi}{dx}|_{x=0^-} - \frac{d\phi}{dx}|_{x=0^+} = 2\phi(0)$$

And:

$$\phi(x = 0^-) = \phi(x = 0^+)$$

For E¡0:

$$A_L e^{-\alpha x} \qquad A_R e^{-\alpha x}$$
$$B_L e^{\alpha x} \qquad B_R e^{\alpha x}$$

Wave function left of the potential is $\phi_L = A_L e^{-\alpha x} + B_L e^{\alpha x}$ and the wave function right of the potential is $\phi_R = A_R e^{-\alpha x} + B_R e^{\alpha x}$. Using this we can apply the previously established conditions to our wave function:

$$\phi_R\left(\frac{d}{2}\right) = C\phi_L\left(\frac{-d}{2}\right)$$

$$\therefore A_R e^{-\alpha\frac{d}{2}} + B_R e^{\alpha\frac{d}{2}} = C(A_L e^{-\alpha\frac{d}{2}} + B_L e^{\alpha\frac{d}{2}})$$

We rewrite this in a nicer notation such that $v = e^{\alpha\frac{d}{2}}$

$$1) \quad \frac{A_R}{v} + B_R v = C(\frac{A_L}{v} + B_L v)$$

Similarly for the rest of our conditions:

$$\frac{d\phi}{dx}(x) = \frac{d\phi}{dx}(x+d)$$

$$\implies \frac{-A_r\cancel{\alpha}}{v} + B_R\cancel{\alpha}v = C(-\cancel{\alpha}A_L v + \cancel{\alpha}\frac{B_L}{v})$$

$$\implies 2) \quad \frac{-A_r}{v} + B_R v = C(-A_L v + \frac{B_L}{v})$$

$$\phi(x = 0^-) = \phi(x = 0^+)$$

$$\implies 3) \quad A_L + B_L = A_R + B_R$$

$$\frac{d\phi}{dx}|_{x=0^-} - \frac{d\phi}{dx}|_{x=0^+} = 2\phi(0)$$

$$\implies 4) \quad [-A_L\alpha + B_L\alpha] - [-A_R\alpha + B_R\alpha] = 2[A_L + B_L]$$

Now we can add 1) and 2):

$$2B_R v = 2C\frac{B_L}{v} \implies B_R = \frac{C}{v^2}B_L$$

And Subtract 1) and 2):

$$\frac{2A_R}{v} = 2CA_L v \implies A_R = Cv^2 A_L$$

Substitution these values for B_R and A_R into 3):

$$A_L + B_L = C(v^2 A_L + \frac{1}{v^2}B_L)$$

$$\implies (Cv^2 - 1)A_L = (1 - \frac{c}{v^2})B_L$$

Converting 4) and substituting values for B_R and A_R thus becomes:

$$A_R\alpha - B_R\alpha = (2+\alpha)A_L + (2-\alpha)B_L = C(v^2\alpha A_L - \frac{1}{v^2}\alpha B_L)$$

$$\implies (\frac{2}{\alpha} + 1)A_L + (\frac{2}{\alpha} - 1)B_L = C[v^2 A_L - \frac{1}{v^2}B_L]$$

$$\implies (Cv^2 - 1 - \frac{2}{\alpha})A_L = (\frac{2}{\alpha} - 1 + \frac{C}{v^2})B_L$$

Using 3):

$$\implies (Cv^2 - 1 - \frac{2}{\alpha})(1 - \frac{C}{v^2}) = (\frac{2}{\alpha} - 1 + \frac{C}{v^2})(Cv^2 - 1)$$

$$\implies Cv^2 - 1\cancel{\frac{2}{\alpha}} - C^2 + \frac{C}{v^2} + \frac{2C}{\alpha v^2} = \frac{2Cv^2}{\alpha} - Cv^2 + C^2\cancel{\frac{2}{\alpha}} + 1 - \frac{C}{v^2}$$

$$\implies 2C^2 + 2 = 2Cv^2 + \frac{2C}{v^2} + \frac{2C}{\alpha v^2} - \frac{2Cv^2}{\alpha}$$

$$\implies C^2 + 2 = Cv^2 + \frac{C}{v^2} + \frac{C}{\alpha v^2} - \frac{Cv^2}{\alpha}$$

$$\implies \frac{1}{2}\left[e^{i\frac{2\pi k}{N}} + e^{-i\frac{2\pi k}{N}} = e^{\alpha d} + e^{-\alpha d} - \frac{1}{\alpha}(e^{\alpha d} - e^{-\alpha d})\right]$$

Finally, by converting this through identities we arrive at the equation for the solutions:

$$cos(\frac{2\pi k}{N}) = cosh(\alpha d) - \frac{1}{\alpha}sinh(\alpha d)$$

Let's examine this equation a bit further by trying to plot both the left-hand-side (LHS) and the right-hand-side (RHS) with respect to alpha.

The LHS is just going to be a straight line, since it does not depend on alpha but rather just on which k we are examining.

The RHS can be understood better by taking the derivative with respect to alpha:

$$\frac{d}{d\alpha}(RHS) = \frac{1}{2}d(e^{\alpha d} - e^{-\alpha d}) + \frac{1}{2\alpha^2}(e^{\alpha d} - e^{-alphad}) - \frac{d}{2\alpha}(e^{\alpha d} + e^{-alphad})$$

$$= (d + \frac{1}{\alpha^2})sinh(\alpha d) - \frac{dcosh(\alpha d}{\alpha}$$

$$= (d + \frac{1}{\alpha^2})(\alpha d + \frac{\alpha^3 d^3}{6} + ...) - \frac{d}{\alpha}(1 + \frac{\alpha^2 d^2}{2} + ...)$$

If d$<$ 1, we only have $< N$ solutions.

If d$>$ 2, we will have $\geq N$ solutions.

As N$\rightarrow \infty$, more lines from the LHS, meaning more continuous.

Extending this to bound and unbound states (so far we've just looked at alpha not beta):

Bound States ("valence e-"):

$$\frac{-d}{2} \leq x \leq 0 : \qquad \phi(x) = A_L e^{\alpha x} + B_L e^{-\alpha x}$$

$$0 \leq x \leq \frac{d}{2} : \qquad \phi(x) = A_R e^{\alpha x} + B_R e^{-\alpha x}$$

Unbound States ("conduction band e-"):

$$\frac{-d}{2} \leq x \leq 0 : \qquad \phi(x) = A_L e^{i\beta x} + B_L e^{-i\beta x}$$

$$0 \leq x \leq \frac{d}{2}: \qquad \phi(x) = A_R e^{i\beta x} + B_R e^{-i\beta x}$$

By defining this β term, where if we wanted to write it instead still as α would be $\alpha = i\beta$, we can solve for the "unbound" states as well. This means that for any given d and N, we should be able to solve for all α_k and all β_k.

So, to understand the unbound states better, we'll examine solutions where β is "large". Looking at our solution equation one more in terms of β:

$$cos(\frac{2\pi k}{N}) = cosh(\beta d) - \frac{1}{\beta} sinh(\beta d)$$

In this case:

$$-1 \leq cos(\beta d) \leq 1$$
$$-1 \leq sin(\beta d) \leq 1$$

Additionally:

$$|\frac{1}{\beta} sin(\beta d)| \leq |cos(\beta d)|$$
$$\implies cos(\beta d) - \frac{1}{\beta} sin(\beta d) \approx cos(\beta d)$$
$$\therefore cos(\frac{2\pi k}{N} = cos(\beta d)$$
$$\implies \beta d = \frac{2\pi k}{N}$$
$$\therefore \beta = \frac{2\pi k}{Nd} = \frac{2\pi k}{L}$$

Since the wave function for β is defined as $e^{\pm i\beta x}$ this becomes $\phi = e^{\pm \frac{2\pi k}{L}}$ which is called the "free particle/wave limit" and whether it is more particle-like or wave-like (aka whether it will disperse or not) is dependent on its mass.

Going back to analyzing the derivative of the RHS for bound states. We already established:

$$0 = (d + \frac{1}{\alpha^2}) sinh(\alpha d) - \frac{d}{\alpha} cosh(\alpha d)$$
$$\implies tanh(\alpha d) = \frac{\frac{d}{\alpha}}{d + \frac{1}{\alpha^2}} = \frac{\alpha d}{\alpha^2 d + 1}$$

We will call this $f(\alpha)$:

$$\frac{df}{d\alpha} = \frac{d}{\alpha^2 d + 1} - \frac{2\alpha^2 d^2}{(\alpha^2 d + 1)^1}$$

We'll set this equal to 0 to find our maximum location:

$$\frac{df}{d\alpha} = 0$$

$$\implies d(\alpha^2 d + 1) = 2\alpha^2 d^2$$

$$\implies \alpha = \frac{1}{\sqrt{d}}$$

Plug this maximum location back into $f(\alpha)$:

$$\tanh(\frac{1}{\sqrt{d}}d) = \frac{\sqrt{d}}{2}$$

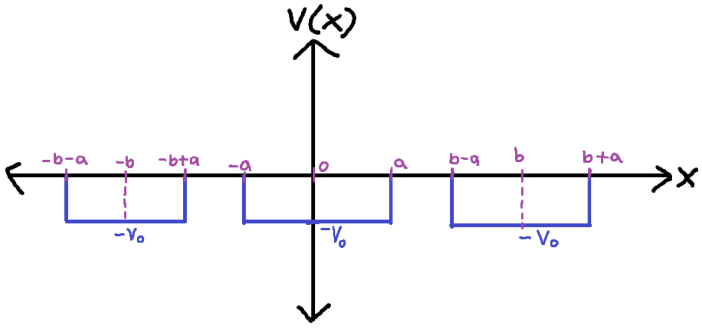
This shows that for small d the RHS of the bound state is monotonic (meaning it keeps on increasing or keeps on decreasing. Alternatively, it has one minimum for large d's.

Quantum Mechanics- Part 3

Melanie Frolich

November 2023

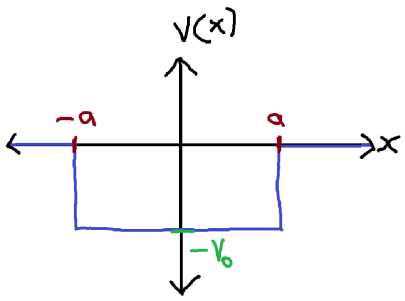
1 Building to Multiple Attractive Centers/Wells



This 1-dimensional model with multiple attractive wells, often called the Kronig-Penney model, starts to build a basic understanding of conductors and insulators and why they work like they do. Our goal is to work towards understanding of this model step by step.

How do you find the changes in energy for a model like this one? We're going to start by expanding on our understanding of a single attractive center and working with it as a delta function confined to a single region in space as opposed to a square well.

1.1 Understanding One Attractive Center



Due to dealing with an attractive potential in a bound state, every solution has to satisfy (where Total Energy is $-E$ and the potential depth is $-V_0$):

$$0 < E < V_0$$

The area of each square well is $2V_0a$, meaning:

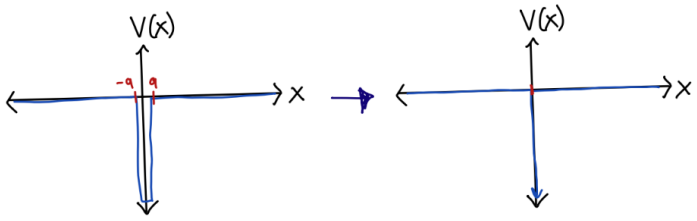
$$\int_{-a}^{a} V(x)dx = -2C$$

where $C = V_0a$

This means that, in a sense:

$$"V(x) = -2C\delta(x)"$$

We can conceptualize this as taking the potential well and compressing its entire area to a single point, x=0. The depth would become infinitely deep and the width would become infinitely narrow:



Plugging this into the wave equation:

$$"\frac{-\hbar^2}{2m}\frac{d^2\phi}{dx^2} - 2c\delta(x)\phi(x) = -E\phi(x)"$$

(where remember $-E = Energy$ and $\phi(x,t) = e^{\frac{iE}{\hbar}t}\phi(x)$

Rewriting this:

$$\implies \frac{d^2\phi}{dx^2} + \frac{4mc}{\hbar^2}\delta(x)\phi(x) = \frac{2mE}{\hbar}\phi(x)$$

$$\implies \frac{d^2\phi}{dx^2} + \frac{4mV_0a}{\hbar^2}\delta(x)\phi(x) = \frac{2mE}{\hbar}\phi(x)$$

$$\implies \frac{d^2\phi}{dx^2} + 2g\delta(x)\phi(x) = \alpha^2\phi(x)$$

where $g = \frac{2mV_0a}{\hbar^2} > 0$ and $\alpha^2 = \frac{2mE}{\hbar} > 0$

So, based on this, is ϕ continuous as x=0?

Well, if ϕ is discontinuous at x=0, then $\frac{d\phi}{dx}|_{x=0}$ has to be $\delta(x)$ and $\frac{d^2\phi}{dx^2}|_{x=0}$ will be "worse" (even harder to define) than $\delta(x)$. Therefore, ϕ has to be continuous at x=0.

Is $\frac{d\phi}{dx}$ continuous at x=0?

No, and the jump must "match" $\delta(x)$ in the potential term!

What about away from x=0?

Away from x=0, the wave equation simplifies to the following (because $V(0 < x < 0) = 0$:

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Therefore the wave function will look as follows (taking into account the need to normalize the probability function)

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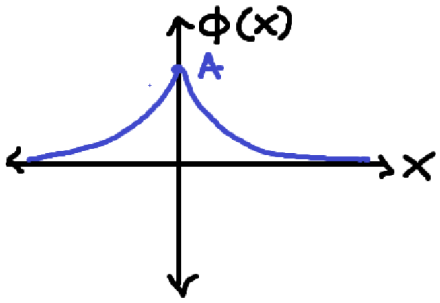
$$x \geq 0: \qquad \phi(x) = Ae^{-\alpha x}$$

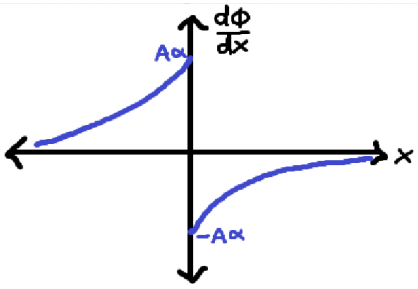
Therefore at $x = 0$, $\phi(x) = A$



And the derivative would look like this:

$$x < 0: \qquad \frac{d\phi(x)}{dx} = A\alpha e^{\alpha x}$$

$$x > 0: \qquad \frac{d\phi(x)}{dx} = -A\alpha e^{-\alpha x}$$



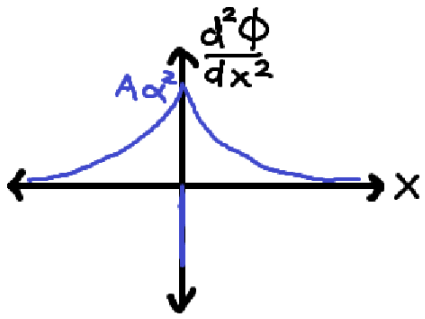
The second derivative would thus look like this:

$$x < 0: \qquad \frac{d^2\phi(x)}{dx^2} = A\alpha^2 e^{\alpha x}$$

$$x > 0: \qquad \frac{d^2\phi(x)}{dx^2} = A\alpha^2 e^{-\alpha x}$$

$$+B\delta(x)$$

**Note: This added delta function exists through all of the 1-D space.



Since $\frac{d\phi}{dx}$ jumps from positive to negative, this can be conceptualized as a very, very negative slope at this point, meaning that there is a negative area at x=0, a delta function where $B < 0$. Another way to conceptualize this is that since $\frac{d\phi}{dx}$ represents the integral of $\frac{d^2\phi}{dx^2}$ then there must be some negative area at x=0 to see that $\frac{d\phi}{dx}$ changes from positive to negative after x=0.

Let's understand the integral of this second derivative:

$$\int_{-\infty}^{\infty} \frac{d^2\phi}{dx^2} dx = \frac{d\phi}{dx}|_{x=\infty} - \frac{d\phi}{dx}|_{x=-\infty}$$

$$A\alpha^2 \int_{-\infty}^{0} e^{\alpha x} dx + A\alpha^2 \int_{0}^{\infty} e^{-\alpha x} dx + B \int_{-\infty}^{\infty} \delta(x) dx = -A\alpha e^{-\alpha x}|_{x=\infty}$$

$$\implies 2A\alpha + B = 0$$

$$\implies B = -2A\alpha$$

With this result, we go back to examining the wave function at x=0 to see if we can discern more about the problem:

$$"\alpha^2\phi(x) = \frac{d^2\phi}{dx^2} + 2g\delta(x)\phi(x)"$$

Integrate this:

$$\alpha^2 A \int_{-\infty}^{0} e^{\alpha x} dx + \alpha^2 A \int_{0}^{\infty} e^{-\alpha x} dx = \int_{-\infty}^{\infty} \frac{d^2\phi}{dx^2} dx + 2g \int_{-\infty}^{\infty} \delta(x)\phi(x) dx$$

$$\implies \alpha A e^{\alpha x}|_{-\infty}^{0} - \alpha A e^{-\alpha x}|_{0}^{\infty} = 0 + 2g\phi(0)$$

$$\implies 2\alpha A = 2gA$$

$$\implies \alpha = g$$

We can thus write the probability function as:

$$x \leq 0 : \qquad P(x) = A^2 e^{2gx}$$

$$x \geq 0 : \qquad P(x) = A^2 e^{-2gx}$$

And we can use to the fact that $\int_{-\infty}^{\infty} P(x)dx = 1$ to find solve for A^2:

$$\frac{2A^2}{2g} = 1$$

$$\implies A^2 = g$$

Therefore we can rewrite the $\phi(x)$ solution as:

$$x \leq 0 : \qquad \phi(x) = \sqrt{g}e^{gx}$$
$$x \geq 0 : \qquad \phi(x) = \sqrt{g}e^{-gx}$$

Remember that g is related to the potential of the well:

$$g = \frac{2mV_0 a}{\hbar^2}$$

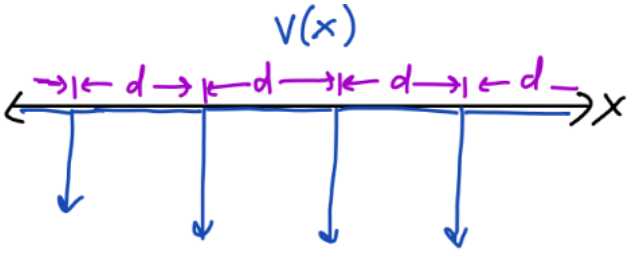
And the bigger the g the more "localized" the solution. This makes sense because you are saying that the stronger the potential, the more likely that the wave function is found there.

So, a summary of how we solved this single Dirac Delta function potential well:

1) $\phi(x)$ for $x > 0$ and $x < 0$
2) Make $\phi(x)$ continuous at x=0 (because it has to be)
3) $\frac{d\phi}{dx}|_{x=0^-} - \frac{d\phi}{dx}|_{x=0^+} = 2g\phi(0)$

1.2 Multiple Wells Along a Line

Let's now imagine we have N number of attractive centers located at $x = d, 2d, ..., nd$, and at each of them there is a dirac delta function ($\delta(x)$) potential energy well.



We set $g = \frac{2mV_0 a}{\hbar^2} = 1$ and furthermore understand the potential energy to be the following sum of different delta potentials:

$$V(x) = -2V_0 a \left[\sum_{n=1}^{N} \delta(x - nd)\right]$$

Much like before, we know that away from the attractive centers the wave equation simplifies to:

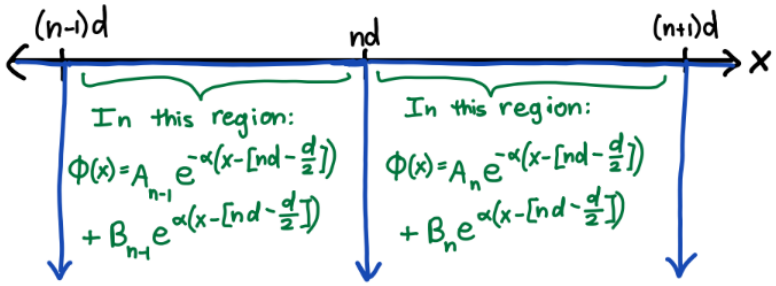
$$\frac{d^2\phi}{dx^2} = \alpha^2\phi$$

And at the attractive centers:

$$"\alpha^2\phi(x) = \frac{d\phi^2}{dx^2} + 2\left[\sum_{n=1}^{N}\delta(x-nd)\right]\phi(x)"$$

Why is it quotations marks? Because delta potentials are weird.

First we will look more in depth at what happens away from the attractive centers. On either side of these attractive centers there will be some term of the wave function that corresponds to decay in one direction and another that corresponds to decay in the other direction. Zooming into one of these attractive centers:



We know that since $\phi(x)$ must be continuous at this delta function location ($x = nd$) (just like before with a single delta function potential) we can create the condition:

$$A_{n-1}e^{-\alpha\frac{d}{2}} + B_{n-1}e^{\alpha\frac{d}{2}} = A_n e^{-\alpha\frac{d}{2}} + B_n e^{\alpha\frac{d}{2}}$$

We can rewrite this in a nicer way by defining $v = e^{-\alpha\frac{d}{2}}$:

$$I) \qquad A_{n-1}v + B_{n-1}\frac{1}{v} = A_n\frac{1}{v} + B_n v$$

In addition, much like before, we know that since there is a dirac delta function we know:

$$\frac{d\phi}{dx}|_{x=nd^-} - \frac{d\phi}{dx}|_{x=nd^+} = 2\phi(nd)$$

Rewritten this becomes:

$$\left[-\alpha A_{n-1}v + \alpha B_{n-1}\frac{1}{v}\right] - \left[-\alpha A_n\frac{1}{v} + \alpha B_n v\right] = 2A_{n-1}v + 2B_{n-1}\frac{1}{1}$$

$$\implies A_{n-1}(-\alpha v - 2v) + B_{n-1}(\frac{\alpha}{v} - \frac{2}{v}) = -\alpha A_n\frac{1}{v} + \alpha B_n v$$

$$\implies \quad II) \qquad -vA_{n-1}(1+\tfrac{2}{\alpha}) + \tfrac{1}{v}B_{n-1}(1-\tfrac{2}{\alpha}) = -A_n\tfrac{1}{v} + B_n v$$

Adding I) and II):

$$\cancel{2}B_n v = \frac{-\cancel{2}v}{\alpha}A_{n-1} + (\frac{\cancel{2}}{v} - \frac{\cancel{2}}{\alpha v})B_{n-1}$$

Subtracting I) and II):

$$\cancel{2}A_n\frac{1}{v} = (\cancel{2}\pi + \frac{\cancel{2}v}{\alpha})A_{n-1} + \frac{\cancel{2}}{\alpha v}B_{n-1}$$

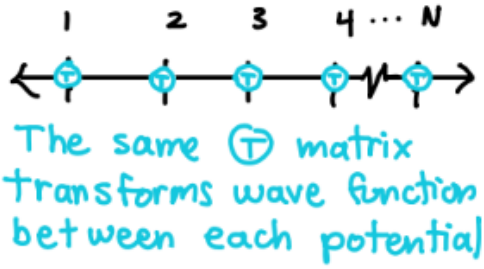
Therefore:

$$B_n = \frac{-1}{\alpha}A_{n-1} + \frac{1}{v^2}(1-\frac{1}{\alpha})B_{n-1}$$
$$A_n = v^2(1+\frac{1}{\alpha})A_{n-1} + \frac{1}{\alpha}B_{n-1}$$

Or, written in matrix format:

$$\begin{pmatrix} A_n \\ B_n \end{pmatrix} = \begin{pmatrix} v^2(1+\frac{1}{\alpha}) & \frac{1}{\alpha} \\ \frac{-1}{\alpha} & \frac{1}{v^2}(1-\frac{1}{\alpha}) \end{pmatrix} \begin{pmatrix} A_{n-1} \\ B_{n-1} \end{pmatrix}$$

We will name this transformation matrix from A_{n-1} and B_{n-1} to A_n and B_n as $T(\alpha, d)$. Note that this matrix has no dependence on which of the N attractive centers we are transforming to or from. This means that we can imagine that for each attractive center there exists this same transformation matrix that transforms from one side of it to the other, like so:



And thus for the total scenario of N attractive centers we end up with:

$$\begin{pmatrix} A_N \\ B_N \end{pmatrix} = T^N \begin{pmatrix} A_0 \\ B_0 \end{pmatrix}$$

However, looking at the image we know that at the ends of the wave function, as it approaches ∞ and $-\infty$ the function must approach 0. This means that this matrix simplifies to:

$$\begin{pmatrix} A_N \\ 0 \end{pmatrix} = \begin{pmatrix} (T^N)_{11} & (T^N)_{12} \\ (T^N)_{21} & (T^N)_{22} \end{pmatrix} \begin{pmatrix} 0 \\ B_0 \end{pmatrix}$$

Yielding the two equations:

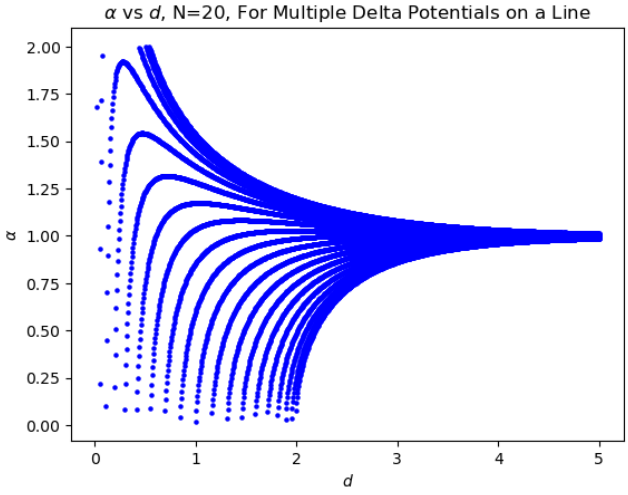
$$A_n = (T^N)_{12} B_0$$

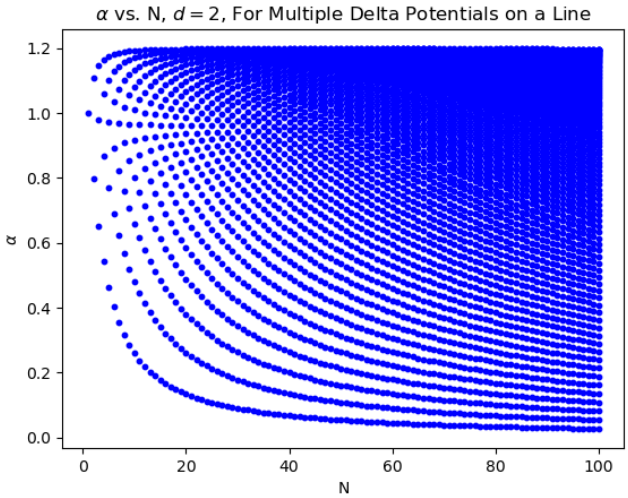
$$0 = (T^N)_{22} B_0$$

We know that $B_0 \neq 0$ for the wave function to actually exist so $(T^N)_{22} = 0$.

1.3 Examples of Graphing the Solutions for Evenly Spaced Delta Function Potentials on a Circle

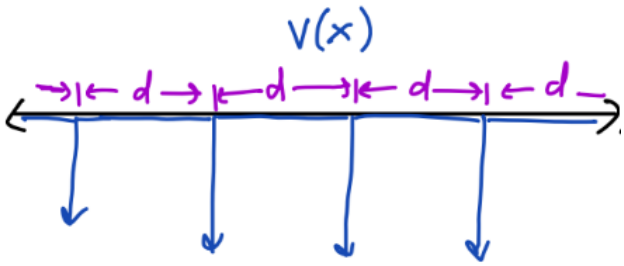
This Transformation matrix was coded in Python and examples of some of the resulting plots are shown below:

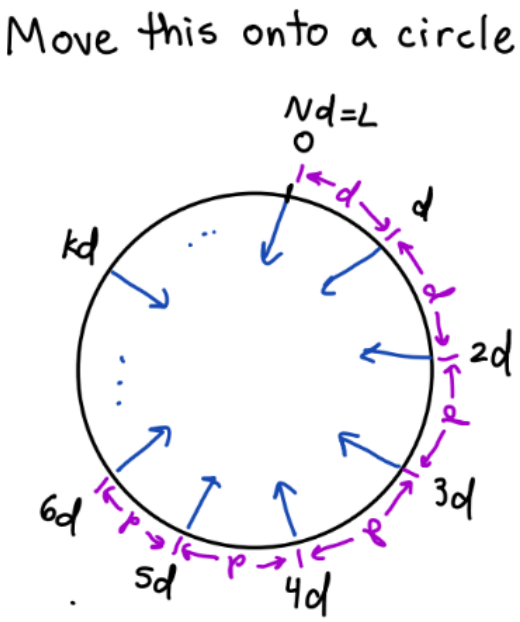




1.4 Putting Them On a Circle

So far, we have been imagining our wells on an infinite flat line. However, there are benefits to instead modeling these potential wells as existing on a circle. A circle, due to its geometry, additionally repeats after a certain length intrinsically due to its shape:





This circle has circumference L, divided into N segments of d length.

$$Nd = L$$

We go back to this position after this length:

$$x = x + L = x + Nd$$

Since there are potential wells of the same depth every d, we can also state that:

$$V(x+L) = V(x)$$
$$V(x+d) = V(x)$$

Previously, for our flat line we had the restriction that $\int_0^L \psi^2(x)dx = 1$. We extending this flat line L out towards infinity, meaning $\int_{-\infty}^{\infty} \psi^2(x)dx = 1$ which further has the consequence that the ends of our wave function must go towards zero ($\psi(-\infty) = \psi(\infty) = 0$).

However, with the circle, we no longer have this restriction on the ends, yet, when making the length L go to ∞, this circle turns into a flat line at any point anyways.

.....

Definition of "Bound"

Before, we had one or multiple attractive potentials, and said the wave function was "bound" thus it didn't exist at the edges (approaching $-\infty$ and ∞). Now, with this model on a circle, "bound" refers simply to attractive centers existing.

.....

Going back to the modified wave equation we used previously but this time looking for solutions of the type $\psi(x,t) = e^{\frac{-iE}{\hbar}t}\phi(x)$ (Notice we are no longer changing the sign of E as we did previously):

$$-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\phi(x) - V(x)\phi(x) = -E\phi(x)$$
$$\implies -\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\phi(x) = V(x)\phi(x) - E\phi(x)$$

Where Energy = E and $E > 0$

Our periodic boundary conditions due to the geometry of the circle are:

$$\phi(x) = \phi(x+L)$$
$$\frac{d\phi}{dx}(x) = \frac{d\phi}{dx}(x+L)$$
$$V(x) = V(x+L)$$

Given the first condition, plugging x into the left hand side of the above Schrodinger wave equation should give the same result as plugging in x+L, meaning:

$$\frac{d^2\phi}{dx^2}(x) = \frac{d^2\phi}{dx^2}(x+L)$$

In addition to these periodic boundary conditions for this circle, we have a set of conditions for the particular problem type we want to solve:

$$V(x) = V(x+d)$$
$$Nd = L$$

This all begs the question of whether $\phi(x) = \phi(x+d)$?
Comparing:

$$-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\phi(x) = V(x)\phi(x) - E\phi(x)$$

And:

$$-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\phi(x+d) = V(x+d)\phi(x+d) - E\phi(x+d) = V(x)\phi(x+d) - E\phi(x+d)$$

It is apparent that $\phi(x+d) = \phi(x)$

$$\therefore \phi(x+2d) = C\phi(x+d) = C^2\phi(x)$$
$$\phi(x+kd) = C^k\phi(x)$$
$$\phi(x+Nd) = C^N\phi(x) = \phi(x)$$
$$\implies C^N = 1 = e^{i2\pi k}$$
$$\implies C = e^{\frac{i2\pi}{N}k}$$

Where k=0,1,2,..,N-1
Therefore, for $\phi(x+Nd)$ when N=1,

$$\phi(x+d) = C\phi(x) = e^{\frac{i2\pi k}{N}}\phi(x)$$
$$\frac{d\phi(x+d)}{dx} = e^{\frac{i2\pi k}{N}}\frac{d\phi(x)}{dx}$$

Looking once more at the wave equation:

$$\frac{d^2\phi}{dx^2} - \frac{2m}{\hbar^2}V(x)\phi(x) = \frac{-2mE}{\hbar^2}\phi(x)$$

We can define two values for total energy in natural units depending on whether the energy is negative or positive:

$$E < 0: \qquad \alpha^2 = \frac{-2mE}{\hbar^2}$$
$$E > 0: \qquad -\beta^2 = \frac{-2mE}{\hbar^2}$$

If $x \neq 0$:

$$E < 0: \qquad \frac{d\phi}{dx} = \alpha^2 \phi$$

$$E > 0: \qquad \frac{d\phi}{dx} = -\beta^2 \phi$$

And at $x = 0$ we have the following δ-function condition:

$$\frac{d\phi}{dx}|_{x=0^-} - \frac{d\phi}{dx}|_{x=0^+} = 2\phi(0)$$

And:

$$\phi(x = 0^-) = \phi(x = 0^+)$$

For $E < 0$, to the left of a given delta potential we have (just like before):

$$A_L e^{-\alpha x} + B_L e^{\alpha x}$$

And on the right:

$$A_R e^{-\alpha x} + B_R e^{\alpha x}$$

Using this we can apply the previously established conditions to our wave function:

$$\phi_R\left(\frac{d}{2}\right) = C\phi_L\left(\frac{-d}{2}\right)$$

$$\therefore A_R e^{-\alpha \frac{d}{2}} + B_R e^{\alpha \frac{d}{2}} = C(A_L e^{-\alpha \frac{d}{2}} + B_L e^{\alpha \frac{d}{2}})$$

We rewrite this in a nicer notation such that $v = e^{\alpha \frac{d}{2}}$

$$1) \quad \frac{A_R}{v} + B_R v = C(\frac{A_L}{v} + B_L v)$$

Similarly for the rest of our conditions:

$$\frac{d\phi}{dx}(x) = \frac{d\phi}{dx}(x + d)$$

$$\implies \frac{-A_r \cancel{\alpha}}{v} + B_R \cancel{\alpha} v = C(-\cancel{\alpha} A_L v + \cancel{\alpha} \frac{B_L}{v})$$

$$\implies 2) \quad \frac{-A_r}{v} + B_R v = C(-A_L v + \frac{B_L}{v})$$

$$\phi(x = 0^-) = \phi(x = 0^+)$$

$$\implies 3) \quad A_L + B_L = A_R + B_R$$

$$\frac{d\phi}{dx}|_{x=0^-} - \frac{d\phi}{dx}|_{x=0^+} = 2\phi(0)$$

$$\implies 4) \quad [-A_L\alpha + B_L\alpha] - [-A_R\alpha + B_R\alpha] = 2[A_L + B_L]$$

Now we can add 1) and 2):

$$2B_R v = 2C\frac{B_L}{v} \implies B_R = \frac{C}{v^2}B_L$$

And Subtract 1) and 2):

$$\frac{2A_R}{v} = 2CA_L v \implies A_R = Cv^2 A_L$$

Substitution these values for B_R and A_R into 3):

$$A_L + B_L = C(v^2 A_L + \frac{1}{v^2}B_L)$$
$$\implies (Cv^2 - 1)A_L = (1 - \frac{c}{v^2})B_L$$

Converting 4) and substituting values for B_R and A_R thus becomes:

$$A_R\alpha - B_R\alpha = (2+\alpha)A_L + (2-\alpha)B_L = C(v^2\alpha A_L - \frac{1}{v^2}\alpha B_L)$$
$$\implies (\frac{2}{\alpha} + 1)A_L + (\frac{2}{\alpha} - 1)B_L = C[v^2 A_L - \frac{1}{v^2}B_L]$$
$$\implies (Cv^2 - 1 - \frac{2}{\alpha})A_L = (\frac{2}{\alpha} - 1 + \frac{C}{v^2})B_L$$

Using 3):

$$\implies (Cv^2 - 1 - \frac{2}{\alpha})(1 - \frac{C}{v^2}) = (\frac{2}{\alpha} - 1 + \frac{C}{v^2})(Cv^2 - 1)$$

$$\implies Cv^2 - 1 \cancel{- \frac{2}{\alpha}} - C^2 + \frac{C}{v^2} + \frac{2C}{\alpha v^2} = \frac{2Cv^2}{\alpha} - Cv^2 + C^2 \cancel{- \frac{2}{\alpha}} + 1 - \frac{C}{v^2}$$
$$\implies 2C^2 + 2 = 2Cv^2 + \frac{2C}{v^2} + \frac{2C}{\alpha v^2} - \frac{2Cv^2}{\alpha}$$
$$\implies C^2 + 2 = Cv^2 + \frac{C}{v^2} + \frac{C}{\alpha v^2} - \frac{Cv^2}{\alpha}$$
$$\implies \frac{1}{2}\left[e^{i\frac{2\pi k}{N}} + e^{-i\frac{2\pi k}{N}} = e^{\alpha d} + e^{-\alpha d} - \frac{1}{\alpha}(e^{\alpha d} - e^{-\alpha d})\right]$$

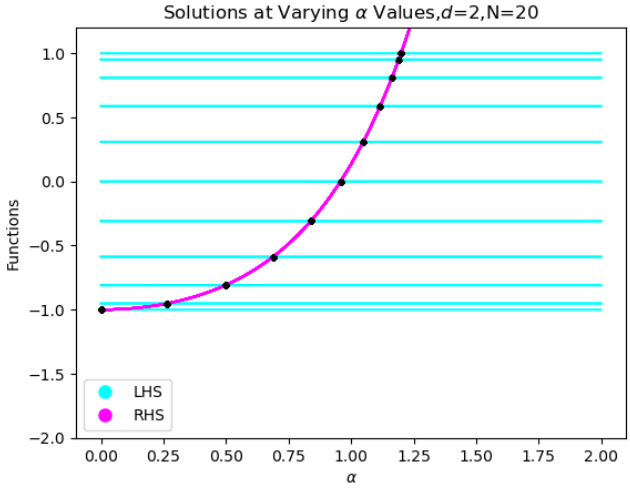
Finally, by converting this through identities we arrive at the equation for the solutions:

$$cos\left(\frac{2\pi k}{N}\right) = cosh(\alpha d) - \frac{1}{\alpha}sinh(\alpha d)$$

Let's examine this equation a bit further by trying to plot both the left-hand-side (LHS) and the right-hand-side (RHS) with respect to alpha.

The LHS is just going to be a straight line, since it does not depend on alpha but rather just on which k we are examining.

An example of this solution plotted looks as follows:



The RHS can be understood better by taking the derivative with respect to alpha:

$$\frac{d}{d\alpha}(RHS) = \frac{1}{2}d(e^{\alpha d} - e^{-\alpha d}) + \frac{1}{2\alpha^2}(e^{\alpha d} - e^{-alphad}) - \frac{d}{2\alpha}(e^{\alpha d} + e^{-alphad})$$

$$= (d + \frac{1}{\alpha^2})sinh(\alpha d) - \frac{dcosh(\alpha d}{\alpha}$$

$$= (d + \frac{1}{\alpha^2})(\alpha d + \frac{\alpha^3 d^3}{6} + ...) - \frac{d}{\alpha}(1 + \frac{\alpha^2 d^2}{2} + ...)$$

If d$<$ 1, we only have $< N$ solutions.
If d$>$ 2, we will have $\geq N$ solutions.
As N$\rightarrow \infty$, more lines from the LHS, meaning more continuous.

Extending to Unbound States

We can also extend this same idea to the unbound states (so far we've just looked at alpha not beta). Both of our wave functions look like this:

Bound States :

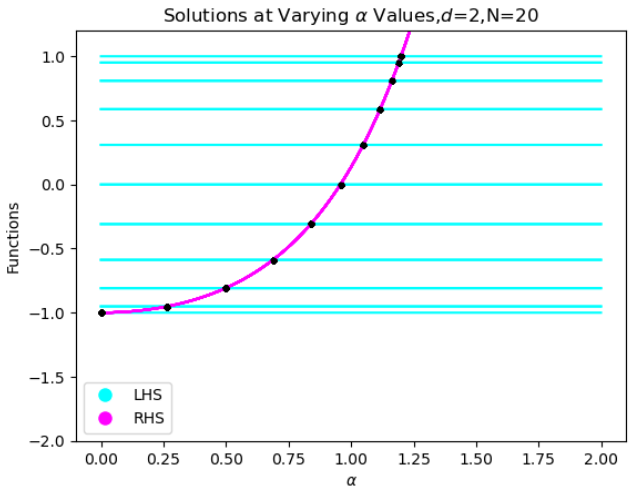
Can be conceptualized as "valence e-" for a metal:

$$\frac{-d}{2} \leq x \leq 0 : \qquad \phi(x) = A_L e^{\alpha x} + B_L e^{-\alpha x}$$

$$0 \leq x \leq \frac{d}{2} : \qquad \phi(x) = A_R e^{\alpha x} + B_R e^{-\alpha x}$$

Equation of Solutions:

$$cos\left(\frac{2\pi k}{N}\right) = cosh(\alpha d) - \frac{1}{\alpha} sinh(\alpha d)$$



Unbound States :

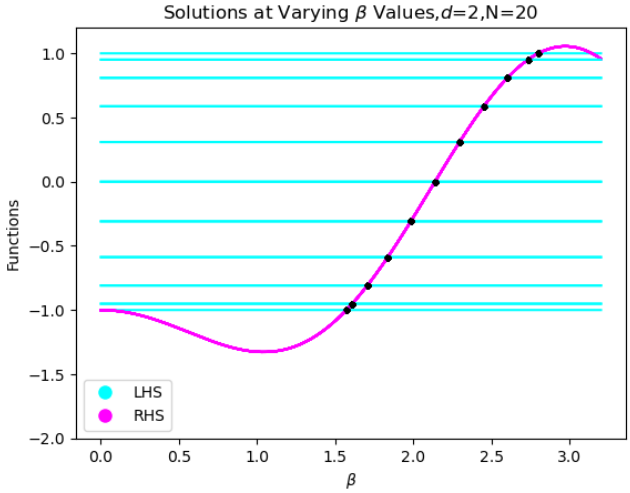
Can be conceptualized as "conduction band e-" for a metal

$$\frac{-d}{2} \leq x \leq 0 : \qquad \phi(x) = A_L e^{i\beta x} + B_L e^{-i\beta x}$$

$$0 \leq x \leq \frac{d}{2} : \qquad \phi(x) = A_R e^{i\beta x} + B_R e^{-i\beta x}$$

Equation of Solutions:

$$cos\left(\frac{2\pi k}{N}\right) = cos(\beta d) - \frac{1}{\beta} sin(\beta d)$$



By defining this β term, where if we wanted to write it instead still as α would be $\alpha = i\beta$, we can solve for the "unbound" states. This means that for any given d and N, we should be able to solve for all α_k and all β_k.

Understanding the trajectory of bound equation better

So, to understand the slope of our bound state RHS solution better, we'll examine solutions where β is "large". Looking at our solution equation one more in terms of β:

$$cos\left(\frac{2\pi k}{N}\right) = cosh(\beta d) - \frac{1}{\beta}sinh(\beta d)$$

In this case:

$$-1 \leq cos(\beta d) \leq 1$$
$$-1 \leq sin(\beta d) \leq 1$$

Additionally:

$$|\frac{1}{\beta}sin(\beta d)| \leq |cos(\beta d)|$$
$$\implies cos(\beta d) - \frac{1}{\beta}sin(\beta d) \approx cos(\beta d)$$
$$\therefore cos\left(\frac{2\pi k}{N}\right) = cos(\beta d)$$
$$\implies \beta d = \frac{2\pi k}{N}$$

$$\therefore \beta = \frac{2\pi k}{Nd} = \frac{2\pi k}{L}$$

Since the wave function for β is defined as $e^{\pm i\beta x}$ this becomes $\phi = e^{\pm \frac{2\pi k}{L}}$ which is called the "free particle/wave limit" and whether it is more particle-like or wave-like (aka whether it will disperse or not) is dependent on its mass.

Going back to analyzing the derivative of the RHS for bound states. We already established:

$$0 = (d + \frac{1}{\alpha^2})sinh(\alpha d) - \frac{d}{\alpha}cosh(\alpha d)$$

$$\implies tanh(\alpha d) = \frac{\frac{d}{\alpha}}{d + \frac{1}{\alpha^2}} = \frac{\alpha d}{\alpha^2 d + 1}$$

We will call this $f(\alpha)$:

$$\frac{df}{d\alpha} = \frac{d}{\alpha^2 d + 1} - \frac{2\alpha^2 d^2}{(\alpha^2 d + 1)^1}$$

We'll set this equal to 0 to find our maximum location:

$$\frac{df}{d\alpha} = 0$$

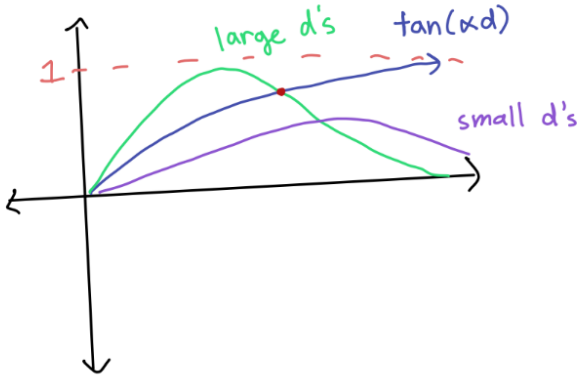
$$\implies d(\alpha^2 d + 1) = 2\alpha^2 d^2$$

$$\implies \alpha = \frac{1}{\sqrt{d}}$$

Plug this maximum location back into $f(\alpha)$:

$$\tanh(\frac{1}{\sqrt{d}}d) = \frac{\sqrt{d}}{2}$$

This shows that for small d the RHS of the bound state is monotonic (meaning it keeps on increasing or keeps on decreasing. Alternatively, it has one minimum for large d's:



Rewriting functions as Taylor's series

Even:

$$cos\left(\frac{2\pi k}{N}\right) = cosh(\alpha d) - \frac{1}{\alpha}sinh(\alpha d) = \left[1 + \frac{\alpha^2 d^2}{2} + \frac{\alpha^4 d^4}{24} + ..\right] - \frac{1}{\alpha}\left[\alpha d + \frac{\alpha^3 d^3}{6} + \frac{\alpha^5 d^5}{120} + ...\right]$$

$$= (1-d) + \frac{\alpha^2 d^2}{6}(3-d) + \frac{\alpha^4 d^4}{120}(5-d) + ...$$

Odd:

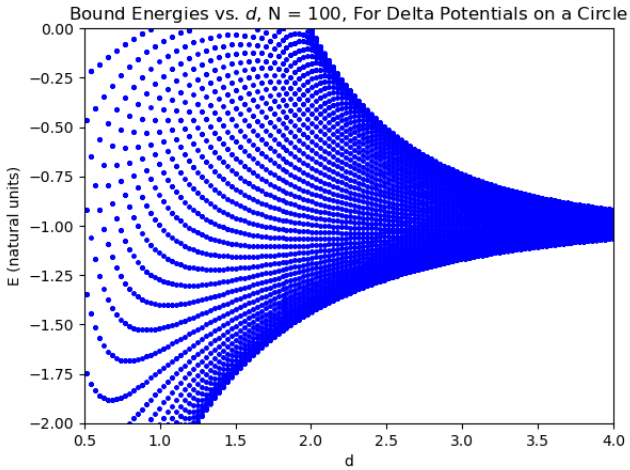
$$cos\left(\frac{2\pi k}{N}\right) = cos(\beta d) - \frac{1}{\beta}sinh(\beta d) = \left[1 - \frac{\beta^2 d^2}{2} + \frac{\beta^4 d^4}{24} - ..\right] - \frac{1}{\beta}\left[\beta d - \frac{\beta^3 d^3}{6} + \frac{\beta^5 d^5}{120} - ...\right]$$

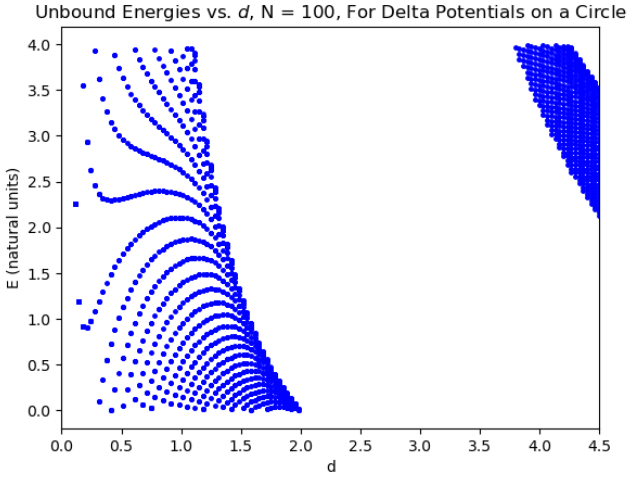
$$= (1-d) - \frac{\beta^2 d^2}{6}(3-d) + \frac{\beta^4 d^4}{120}(5-d) + ...$$

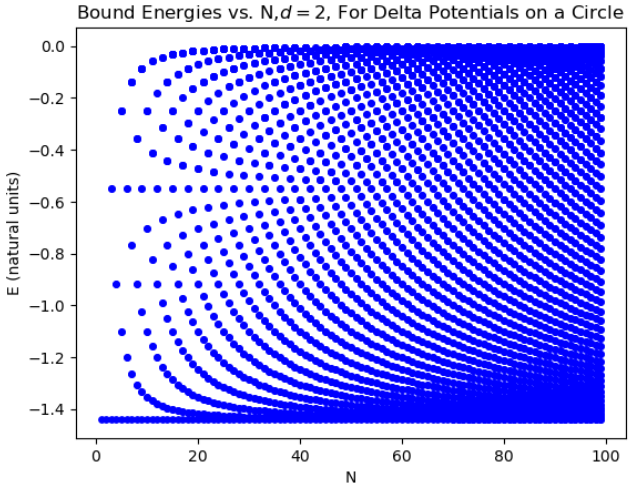
Rewriting these equations in terms of these Taylor's series shows a few things. First it shows what happens when *alpha* or *beta* are 0. The function starts at 1-d. Furthermore, comparing even and odd states shows more clearly why the odd states' RHS fluctuates from top to bottom as we increase β.

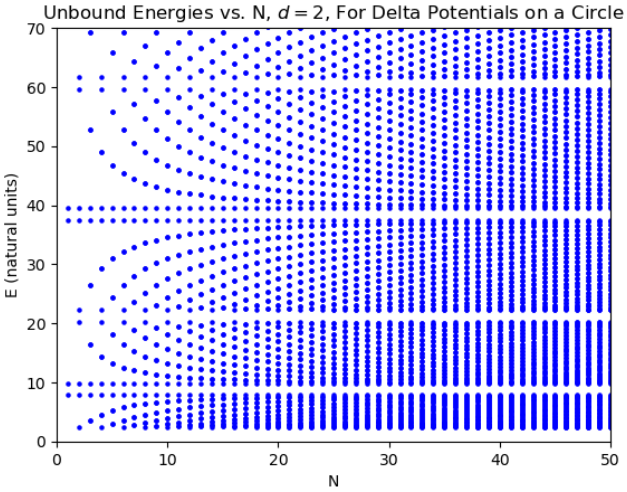
1.5 Examples of Graphing the Solutions for Evenly Spaced Delta Function Potentials on a Circle

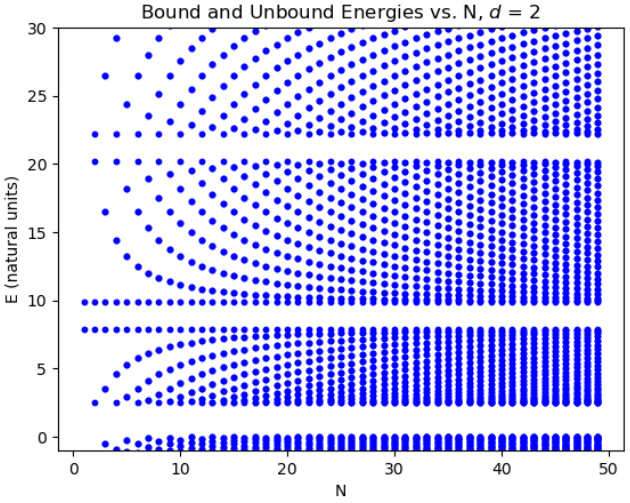
Solutions to the resulting solution equations for bound and unbound states were coded and examples of some of the resulting plots are shown below:

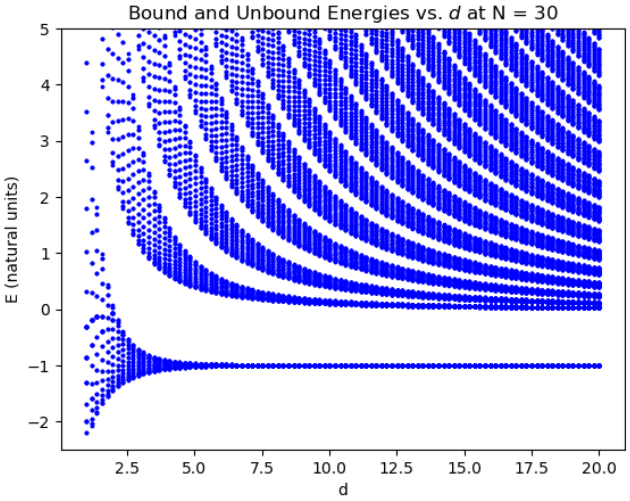



Unbound Energies vs. d, N = 100, For Delta Potentials on a Circle
E (natural units)
d
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5


Bound Energies vs. N,d = 2, For Delta Potentials on a Circle
E (natural units)
N
0.0
−0.2
−0.4
−0.6
−0.8
−1.0
−1.2
−1.4
0
20
40
60
80
100


Unbound Energies vs. N, $d = 2$, For Delta Potentials on a Circle
E (natural units)
N
0
10
20
30
40
50
60
70


Bound and Unbound Energies vs. N, $d = 2$
E (natural units)
N
0
5
10
15
20
25
30
40
50


Bound and Unbound Energies vs. d at N = 30
E (natural units)
d
5
4
3
2
1
0
−1
−2
2.5
5.0
7.5
10.0
12.5
15.0
17.5
20.0

Quantum Mechanics- Part 4

Melanie Frolich

December 2023

1 Quantum Harmonic Oscillator

1.1 Review of Newton's Harmonic Oscillator

The harmonic oscillator in classical mechanics has this potential energy related to the spring constant k:

$$V(x) = \frac{1}{2}kx^2$$

And some force:

$$F(x) = -kx$$

This k is defined as:

$$k > 0$$

$$k \text{ units : } \frac{kg}{sec^2}$$
$$\frac{k}{m} \text{ units: } \frac{1}{sec^2}$$

From the force we find the equation of motion:

$$m\frac{d^2x}{dt^2} = -kx$$

$$\implies \frac{d^2x}{dt^2} = -\frac{k}{m}x$$

We define angular frequency or "natural frequency" of the harmonic oscillator as $\omega = \sqrt{\frac{k}{m}}$ or $k = m\omega^2$

Thus the acceleration becomes:

$$\frac{d^2x}{dt^2} = -\omega^2 x$$

A known solution to this spring equation is:

$$x(t) = Asin(\omega t) + Bcos(\omega t)$$

We can take the derivative of this with respect to time to get velocity:

$$v(t) = A\omega cos(\omega t) - B\omega sin(\omega t)$$

Typically we set $x(0) = x_0$ and $V(0) = V_0$.
Therefore:

$$B = x_0$$

$$A = 0$$

Therefore the position and velocity equations simplify to:

$$x(t) = x_0 cos(\omega t)$$
$$v(t) = -x_0 \omega sin(\omega t)$$

Thus we can rewrite the potential energy of this harmonic oscillator with respect to time instead of position:

$$V(t) = \frac{1}{2}kx^2(t) = \frac{1}{2}kx_0^2 cos^2(\omega t)$$

The kinetic energy will therefore also change in time as:

$$KE(t) = \frac{1}{2}mv^2(t) = \frac{1}{2}mx_0^2\omega^2 sin^2(\omega t) = \frac{1}{2}kx_0^2 sin^2(\omega t)$$

The total energy is thus:

$$TE(t) = \frac{1}{2}kx_0^2\left[cos^2(\omega t) + sin^2(\omega t)\right] = \frac{1}{2}kx_0^2 = constant \geq 0$$

1.2 Quantum Harmonic Oscillator

Now, in quantum mechanics, instead of directly finding the value of the total energy, we use an operator (the Hamiltonian) that when operating on a given wave function yields a value for the energy of that state. The potential energy of the harmonic oscillator is nonetheless the same:

$$\left[\frac{-\hbar^2}{2m}\frac{d^2}{dx^2} + \frac{1}{2}kx^2(x)\right]\phi(x) = E\phi(x)$$

We switch this over to natural units by setting $y = \frac{x}{b} \implies x = by$

This b is chosen as the length in x units at which the kinetic energy and potential energy are the same, and is dictated by the mass and spring constant of the particular model: $\frac{\hbar^2}{2mb^2} = \frac{1}{2}kb^2$.

The units of b should indeed be length, in this case meters, as shown:

$$2mb^2 = \frac{1}{2}m\omega^2 b^2$$

$$\implies b^4 = \frac{\hbar^2}{m^2\omega^2} \implies b^2 = \frac{\hbar}{m\omega} \implies units: \frac{\cancel{kg}\frac{m^2}{\cancel{s}}\cancel{s}}{\frac{\cancel{kg}}{\cancel{s}}}$$

The wave equation using a different wave function, which we will call χ, which is natural units of y thus becomes:

$$\frac{\hbar^2}{2mb^2}\frac{d^2\chi(y)}{dy^2} + \frac{1}{2}kb^2y^2\chi(y) = E\chi(y)$$

$$\frac{-\hbar^{\cancel{2}}}{2\cancel{m}\frac{\cancel{\hbar}}{\cancel{m}\omega}}\frac{d^2\chi(y)}{dy^2}+\frac{1}{2}(\cancel{m}\omega^{\cancel{2}})\frac{\hbar}{\cancel{m}\omega}y^2\chi(y)=E\chi(y)$$

$$\implies \frac{-1}{2}\hbar\omega\frac{d^2\chi}{dy^2}+\frac{1}{2}\hbar\omega y^2\chi(y)=E\chi(y)$$

Therefore E is proportional to $\hbar\omega$, which is also in units of Joules. We can therefore define the energies in terms of the unitless α where $E=\alpha\hbar\omega \implies \alpha=\frac{E}{\hbar\omega}$. Furthermore, we know that this wave equation has n solutions of different functions χ_n with different energies therefore:

$$\implies \frac{-1}{2}\frac{d^2\chi_n}{dy^2}+\frac{1}{2}y^2\chi_n=\alpha_n\chi_n$$

This can also be written in the format of an operator as previously shown:

$$\left[\frac{-1}{2}\frac{d^2}{dy^2}+\frac{1}{2}y^2\right]\chi_n(y)=[\alpha_n]\,\chi_n(y)$$

If $\alpha_n\neq\alpha_m$, then for two different functions:

$$\int_{-\infty}^{\infty}\chi_n^*(y)\chi_m(y)dy=0$$

In order to solve this equation we'll define some operator a:

$$a=\frac{1}{\sqrt{2}}\left[\frac{d}{dy}+y\right]$$

****

Before continuing let's take a small detour to understand a common property taught in linear algebra classes, namely:

$$(AB)^\dagger=(B^\dagger A^\dagger)$$

In Dirac notation, it is clear to see where this comes from:

$$\langle w|\,AB\,|v\rangle=\langle(AB)^\dagger|\,w\,|v\rangle=\langle w|(A(B)v)\rangle=\langle A^\dagger w|Bv\rangle=\langle B^\dagger A^\dagger w|v\rangle$$

****

Now, returning to the operator above, we will try to understand it better by first examining just the $\frac{d}{dx}$ part of it. We can show that $\left(\frac{d}{dx}\right)^\dagger=\frac{-d}{dx}$ based on the following proof:

$$\int_{-\infty}^{\infty}\phi^*(x)\left[\frac{d}{dx}\psi(x)\right]dx=\int_{-\infty}^{\infty}\left[\frac{d}{dx}(\phi^*(x)\psi(x))-(\frac{d}{dx}\phi^*(x))\psi(x)\right]dx$$

$$= \cancel{\phi^*(x)\psi(x)\Big|_{-\infty}^{\infty}} + \int_{-\infty}^{\infty} \left[\frac{-d}{dx}\phi^*(x)\right]\psi(x)dx = \int_{-\infty}^{\infty} \left[\frac{-d}{dx}\phi(x)\right]^*\psi(x)dx$$

This shows that $\frac{d}{dx}$ acting on the unconjugated wave function is the same as conjugated $\frac{-d}{dx}$ acting on the conjugated wave function. In other words, this is an example of a complex conjugate that is Hermitian. If you apply † on this operator twice, you end up where you started.

Therefore, based on the above proof we thus know that:

$$a^\dagger = \frac{1}{\sqrt{2}}\left[\left(\frac{d}{dy}\right)^\dagger + y^\dagger\right] = \frac{1}{\sqrt{2}}\left[\frac{-d}{dy} + y\right]$$

Let's apply both $a^\dagger$ and a to a function and see what happens:

$$(a^\dagger a)f(y) = \frac{1}{\sqrt{2}}\left[\frac{-d}{dy} + y\right]\frac{1}{\sqrt{2}}\left[\frac{d}{dy} + y\right]f(y)$$

$$= \left[\frac{-1}{2}\frac{d^2}{dy^2} + \frac{1}{2}y^2 - \frac{1}{2}\right]f(y)$$

As you can tell, this is quite similar to the wave equation and the operator we are looking for. In fact, we can define α as:

$$\alpha = a^\dagger a + \frac{1}{2}$$

Additionally we'll define:

$$N = a^\dagger a \implies N^\dagger = N$$

With this definition, we can rewrite the wave equation as:

$$N\chi = (\alpha - \frac{1}{2})\chi$$

Now let's look at $aa^\dagger$:

$$aa^\dagger = \frac{-1}{2}\frac{d^2}{dy^2} + \frac{1}{2}y^2 + \frac{1}{2}$$

$$\implies aa^\dagger - a^\dagger a = 1$$

In other words $aa^\dagger - a^\dagger a = I$ (where I is the Identity Matrix) if a is a matrix.

We haven't really defined what a is but we can look at how it works if we define it as a 2x2 matrix:

$$a = \begin{pmatrix} a_{11} & a_{12} \\ a_{21} & a_{22} \end{pmatrix}$$

Therefore:

$$aa^\dagger - a^\dagger a = I$$

$$\begin{pmatrix} a_{11} & a_{12} \\ a_{21} & a_{22} \end{pmatrix} \begin{pmatrix} a_{11}^* & a_{12}^* \\ a_{21}^* & a_{22}^* \end{pmatrix} - \begin{pmatrix} a_{11}^* & a_{12}^* \\ a_{21}^* & a_{22}^* \end{pmatrix} \begin{pmatrix} a_{11} & a_{12} \\ a_{21} & a_{22} \end{pmatrix} = I$$

$$\implies \begin{pmatrix} a_{12}a_{12}^* - a_{21}^* a_{21} & a_{11}a_{21}^* + a_{12}a_{22}^* - a_{11}^* a_{12} - a_{21}^* a_{22} \\ a_{21}a_{11}^* + a_{22}a_{12}^* - a_{12}^* a_{11} - a_{22}^* a_{12} & a_{21}a_{21}^* - a_{12}^* a_{12} \end{pmatrix} = I$$

Since this has to equal the identity matrix, the diagonal values must be equal to 1. This means that the implication if we make a a 2x2 matrix is that $a_{12}a_{12}^* - a_{21}^* a_{21} = 1$ and $a_{21}a_{21}^* - a_{12}^* a_{12} = 1$.

Additionally, based on the fact that $aa^\dagger - a^\dagger a = 1$, the following commutators simplify as follows:

$$[N, a^\dagger] = Na^\dagger - a^\dagger N = a^\dagger aaa^\dagger - a^\dagger a^\dagger a = a^\dagger(aa^\dagger - a^\dagger a) = a^\dagger$$

$$[N, a] = Na - aN = a^\dagger aaa - aa^\dagger a = (a^\dagger a - aa^\dagger)a = -a$$

$$[a, a^\dagger] = aa^\dagger - a^\dagger a = 1$$

We're going to use these properties of a to try to solve for the set of solutions to our wave equation:

Starting once more with:

$$N\chi = (\alpha - \frac{1}{2})\chi$$

We apply the operator/matrix a to this function to get:

$$aN\chi = (\alpha - \frac{1}{2})a\chi$$

Using the previous properties discussed we know that $Na - aN = -a \implies aN = a + Na$. So the wave function becomes:

$$(a + Na)\chi = (\alpha - \frac{1}{2})a\chi$$

$$\implies N[a\chi] = (\alpha - \frac{3}{2})[a\chi]$$

What this is really showing us is that we have found a new solution to this wave equation, where the wave function is $a\chi$ and the eigenvalue that represents the energy is $\alpha - \frac{3}{2}$

Alternatively, if we apply the hermitian conjugate of a ($a^\dagger$) to the wave function we obtain:

$$a^\dagger N\chi = (\alpha - \frac{1}{2})a^\dagger\chi$$

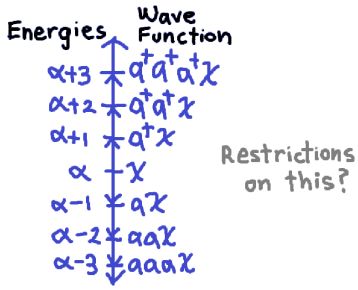
$$(-a + Na^\dagger)\chi = (\alpha - \frac{1}{2})a^\dagger\chi$$

$$\implies N[a^\dagger\chi] = (\alpha + \frac{1}{2})[a^\dagger\chi]$$

Thus, we have found a new solution where the wave function is $a^\dagger\chi$ and the eigenvalue that represents the energy is $\alpha + \frac{1}{2}$

This process of applying either a or $a^\dagger$ can be repeated meaning there is some set of solutions such that as you apply a, the next solution is 1 less than the previous and as you apply $a^\dagger$ the next solution is 1 more than the previous.

Now we have a continuum of solutions to the wave equation and the corresponding energies of these solutions. We know that there should be an infinite number of solutions because we are dealing with energy, however it is still possible that there are restrictions in either of the two directions.



For this we can look at what happens when we normalize the function. Our normalization condition is that $\int_{-\infty}^{\infty} \chi^*\chi dx$ must equal some finite, positive value because it represents the total probability of the particle existing (which we typically normalize to be 1). We will use this our advantage to better understand the limits on the possible solutions and energies by taking the following integral:

$$\int_{-\infty}^{\infty} (a\chi)^*(a\chi)dx = \int_{-\infty}^{\infty} \chi^* a^* a\chi dx$$

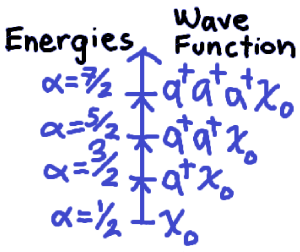
$$= \int_{-\infty}^{\infty} \chi^* N\chi dx = (\alpha - \frac{1}{2}) \int_{-\infty}^{\infty} \chi^*\chi dx \geq 0$$

$$\implies (\alpha - \frac{1}{2}) \geq 0$$

$$\implies \alpha \geq \frac{1}{2}$$

This has the implication that the last non-zero energy value/wave function, χ_0 has the property that $a\chi_0 = 0$. If this weren't the case, $\alpha \geq \frac{1}{2}$ would not be upheld because it would still be possible to find new α values that are negative.

This means that the "eigenvector" χ_0 and its "eigenvalue" α are the stopping point (lowest energy state) for our solution set. The overall solution set would look like this:



The implication of this restriction on χ_0 is that we can solve for it as follows:

$$a\chi_0 = \frac{1}{\sqrt{2}}\left(\frac{d}{dy} + y\right)\chi_0 = 0$$

$$\implies \frac{d}{dy}\chi_0 + y\chi_0 = 0$$

$$\implies \int_{\chi(0)}^{\chi(y)} \frac{d\chi_0}{\chi_0} = -\int_0^y y dy$$

$$\implies ln(\chi_0(y)) - ln(c_0) = \frac{-y^2}{2}$$

$$\implies \chi_0(y) = c_0 e^{\frac{-y^2}{2}}$$

We find the value for χ_0 at $y = 0$ as follows:

$$\int_{-\infty}^{\infty} \chi_0^2 dy = 1 \implies c_0^2 \int_{-\infty}^{\infty} e^{-y^2} dy = 1$$

$$\implies c_0^2\sqrt{\pi} = 1 \implies c_0 = \frac{1}{\pi^{\frac{1}{4}}}$$

$$\implies \chi_0 = \frac{1}{\sqrt{2\pi}} e^{-\frac{y^2}{2}}$$

$$\chi_0 \qquad \alpha = \frac{1}{2}$$

$$a^\dagger\chi_0 \qquad \alpha = \frac{3}{2}$$

$$a^\dagger a^\dagger\chi_0 \qquad \alpha = \frac{5}{2}$$

$$a^\dagger a^\dagger a^\dagger\chi_0 \qquad \alpha = \frac{7}{2}$$

Now we will find the relationship between one solution (energy state) of the wave equation and the next state that is higher in energy.

We start with the premise that a given solution χ_n there will be some value eigenvalue n that corresponds to the operator H (where $n = \alpha - \frac{1}{2}$)

$$N\chi_n = n\chi_n$$

χ_n can be rewritten as $a^\dagger ... a^\dagger \chi_0$ (with n number of $a^\dagger$):

$$N(a^\dagger ... a^\dagger \chi_0) = n(a^\dagger ... a^\dagger \chi_0)$$

We also know that when we apply $a^\dagger$ to one solution/eigenvector, the result is the eigenvector that is one step higher in energy multiplied by some constant:

$$a^\dagger \chi_n = C\chi_{n+1}$$

Using these facts we can perform the normalization integral for χ_{n+1} (we presume that χ_n is already normalized)

$$C^2 \int_{-\infty}^{\infty} \chi_{n+1}^2 dy = \int_{-\infty}^{\infty} (a^\dagger \chi_n)(a^\dagger \chi_n) dy = \int_{\infty}^{\infty} \chi_n (a a^\dagger \chi_n)$$

$$= \int_{\infty}^{\infty} \chi_n ((a^\dagger a + 1)\chi_n) = \int_{\infty}^{\infty} \chi_n [a^\dagger a \chi_n] dy + \int_{-\infty}^{\infty} \chi_n^2 dy = (n+1) \int_{-\infty}^{\infty} \chi_n^2 dy = n+1$$

$$\implies C^2 \int_{-\infty}^{\infty} \chi_{n+1}^2 dy = (n+1) \int_{-\infty}^{\infty} \chi_n^2 dy \implies C^2 = n+1$$

$$\implies C = \sqrt{n+1}$$

So we arrive at (repeating the same process for a operator as well:

$$a^\dagger \chi_n = \sqrt{n+1}\chi_{n+1}$$

$$a\chi_n = \sqrt{n}\chi_{n-1}$$

Therefore, the normalized χ_{n+1} becomes:

$$\chi_{n+1} = \frac{1}{\sqrt{n+1}} a^\dagger \chi_n$$

Now, looking once more at our solution for the lowest energy state χ_0:

$$\chi_0 = \frac{1}{\sqrt{\pi}} e^{\frac{-y^2}{2}}$$

We know the following is true:

$$\frac{d}{dy}\left(\frac{1}{\sqrt{\pi}} e^{\frac{-y^2}{2}}\right) = -\frac{1}{\sqrt{\pi}} y e^{\frac{-y^2}{2}}$$

If we think of this as a polynomial $\frac{1}{\sqrt{\pi}}$ multiplying $e^{\frac{-y^2}{2}}$, then what happens upon taking the derivative is we end up with a new polynomial of +1 higher order multiplying $e^{\frac{-y^2}{2}}$.

We can generalize this for any polynomial as follows:

$$\frac{d}{dy}\left\{H_n(y)e^{\frac{-y^2}{2}}\right\} = \frac{dH_n(y)}{dy}e^{\frac{-y^2}{2}} - yH_n(y)e^{\frac{-y^2}{2}}$$
$$= \left[\frac{dH_n(y)}{dy} - yH_n(y)\right]e^{\frac{-y^2}{2}}$$

Now we have our previous definition of χ_n and our new definition for normalized χ_{n+1}. :

$$\chi_n = \frac{H_n(y)}{\sqrt{2\pi}}e^{\frac{-y^2}{2}}$$

$$\chi_{n+1} = \frac{1}{\sqrt{n+1}}\left(\frac{1}{\sqrt{2}}\right)\left[-\frac{d}{dy} + y\right]\chi_n = \frac{1}{\sqrt{2(n+1)}}\left[-\frac{d\chi_n}{dy} + y\chi_n\right]$$

$$\chi_{n+1} = \frac{1}{\sqrt{2(n+1)}\sqrt{2\pi}}\left[-\frac{d}{dy}(H_n(y)e^{\frac{-y^2}{2}}) + yH_n(y)e^{\frac{-y^2}{2}}\right]$$

From here we can substitute $\chi_{n+1} = \frac{H_{n+1}(y)}{\sqrt{2\pi}}e^{\frac{-y^2}{2}}$:

$$\frac{H_{n+1}(y)}{\cancel{\sqrt{2\pi}}}\cancel{e^{\frac{-y^2}{2}}} = \frac{1}{\sqrt{2(n+1)}\cancel{\sqrt{2\pi}}}\left[-\frac{d}{dy}(H_n(y)\cancel{e^{\frac{-y^2}{2}}}) + yH_n(y)\cancel{e^{\frac{-y^2}{2}}} + yH_n(y)\cancel{e^{\frac{-y^2}{2}}}\right]$$

What we're left with is a relationship from one "Hermite polynomial" to the next:

$$H_{n+1}(y) = \frac{1}{\sqrt{2(n+1)}}\left[-\frac{dH_n(y)}{dy} + 2yH_n(y)\right]$$

Let's examine what these polynomials are when $H_0 = 1$ (even function):
n=0:

$$\sqrt{2}H_1 = \frac{-dH_0}{dy} + 2yH_0 = 0 + 2y$$
$$\implies H_1 = \sqrt{2}y$$

(H_1 is odd function)
n=1:

$$2H_2 = \frac{-dH_1}{dy} + 2yH_1$$
$$\implies 2H_2 = \frac{-d}{dy}(\sqrt{2}y) + 2\sqrt{2}yy = 2\sqrt{2}y^2 - \sqrt{2}$$
$$\implies H_2 = \sqrt{2}y^2 - \frac{1}{\sqrt{2}}$$

(H_2 is even function)
n=2:

$$\sqrt{6}H_3 = \frac{-dH_2}{dy} + yH_2$$

$$\sqrt{6}H_3 = \frac{-d}{dy}(\sqrt{2}y^2 - \frac{1}{\sqrt{2}}) + \sqrt{2}y^3 - \frac{y}{\sqrt{2}}$$

$$\implies H_3 = \frac{1}{\sqrt{3}}y^3 - \left(2\sqrt{2} + \frac{1}{\sqrt{2}}\right)\frac{1}{\sqrt{6}}y$$

(H_3 is an odd function)

As you can tell, these Hermite polynomials alternate between being odd and even functions and increase order each time.

Another interesting thing to note is that the wave functions are orthonormal, meaning that given our chosen inner product:

$$\int_{-\infty}^{\infty} \chi_n(y)\chi_m(y)dy = \delta_{nm}$$

If we rewrite this in terms of the Hermite polynomials:

$$\frac{1}{2\pi}\int_{-\infty}^{\infty} e^{-y^2} H_n(y)H_m(y)dy = \delta_{nm}$$

Therefore we can state that the Hermite polynomials are orthonormal polynomials under a Gaussian weight.

1.3 2-D Classical Harmonic Oscillator

We can expand the harmonic oscillator to 2 dimensions by defining a potential energy that depends on the radius from a point:

$$r^2 = x^2 + y^2$$

$$V(x,y) = \frac{1}{2}kx^2 + \frac{1}{2}ky^2 = \frac{1}{2}k(x^2+y^2) = \frac{1}{2}kr^2$$

Therefore the total energy (refer to central force chapter) becomes:

$$E = \frac{1}{2}m\left(\frac{dr}{dt}\right)^2 + \frac{L^2}{2mr} + \frac{1}{2}kr^2$$

The first two terms are our radial kinetic energy and rotational kinetic energy respectively and L is angular momentum.

$$\implies \frac{dr}{dt} = \sqrt{\frac{2}{m}\left(E - \frac{L^2}{2mr^2} - \frac{1}{2}kr^2\right)}$$

By defining $k = m\omega^2$ where m is mass and ω is angular frequency we arrive at:

$$\frac{r}{\omega}\frac{dr}{dt} = \sqrt{\frac{2E}{m\omega^2}r^2 - \frac{L^2}{m^2\omega^2} - r^4}$$

Now we define $r^2 = u$ and $k = m\omega^2$ where m is mass and ω is angular frequency such that $\frac{du}{dt} = 2r\frac{dr}{dt}$. Through some manipulation and by defining $r^2 = u$ we arrive at:

$$2r\frac{dr}{dt} = \sqrt{\frac{1}{m^2\omega^4}(E^2 - L^2\omega^2) - (u - \frac{E}{m\omega^2})^2}$$

From here, we just notice that everything under the square root must be greater than or equal to zero, which therefore implies that:

$$\frac{1}{m^2\omega^2}(E^2 - L^2\omega^2) \geq 0$$

$$\implies E \geq L\omega$$

Well, what happens if $E = L\omega$? If $E = L\omega$ then that necessitates that $u - \frac{E}{m\omega^2} = 0$, meaning that $u = \frac{E}{m\omega^2}$ and $\frac{du}{dt} = 0$ but this is only in this particular case, the lowest energy possible.

To simplify this problem it is useful to perform a change of variables for energy and time:

$$E = \alpha L\omega$$

$$\tau = \omega t$$

This α defined for energy has a range of $\alpha \geq 1$ because of the restriction we just demonstrated above where $E \geq L\omega$.

Furthermore, since we already established that $u \geq \frac{E}{m\omega^2}$, we will rewrite u as follows where $\beta \geq 1$ and where β is a function of time:

$$u = \beta\frac{E}{m\omega^2} = \beta\alpha\frac{L\omega}{m\omega^2} = \frac{\beta\alpha L}{m\omega}$$

So, having defined all this we rewrite our energy equation once more:

$$\frac{1}{2\omega}\frac{du}{dt} = \sqrt{\frac{1}{m^2\omega^4}(E - L^2\omega^2) - (u - \frac{E}{m\omega})^2}$$

$$\implies \frac{\alpha L}{m\omega}\frac{1}{2}\frac{d\beta}{d\tau} = \sqrt{\frac{L^2\omega^2}{m^2\omega^4}[\alpha^2 - 1] - \frac{\alpha^2 L^2}{m^2\omega^2}[\beta - 1]^2}$$

$$\implies \frac{\alpha \cancel{L}}{\cancel{m\omega}}\frac{1}{2}\frac{d\beta}{d\tau} = \frac{\alpha \cancel{L}}{\cancel{m\omega}}\sqrt{(1 - \frac{1}{\alpha^2}) - (\beta - 1)^2}$$

$$\implies \frac{1}{2}\frac{d\beta}{d\tau} = \sqrt{(1-\frac{1}{\alpha^2}) - (\beta-1)^2}$$

This is now solvable by converting this $\beta(\tau)$ function into a function $r(t)$:

$$\frac{d\beta}{dt} = 2\sqrt{(1-\frac{1}{\alpha^2}) - (\beta-1)^2}$$

We can set $u = \beta - 1$, meaning $du = d\beta$:

$$\implies \frac{1}{2}\int \frac{du}{\sqrt{(1-\frac{1}{\alpha^2}) - u^2}} = \int d\tau$$

$$\implies \frac{1}{2} sin^{-1}\left(\frac{u}{1+\frac{1}{\alpha^2}}\right) = \tau$$

$$\implies \frac{u}{1+\frac{1}{\alpha^2}} = sin(2\tau)$$

$$\implies \frac{\beta-1}{1+\frac{1}{\alpha^2}} = sin(2\tau)$$

$$\beta(\tau) = sin(2\tau)(1+\frac{1}{\alpha^2}) + 1$$

Now, we also set our angular momentum to be in the z direction, meaning that based on the definition of angular momentum as a cross product (in cylindrical coordinates) we can see that:

$$L = mr^2\frac{d\phi}{dt} = mu\frac{d\phi}{dt} = m\alpha\beta\frac{L}{m\omega}\frac{d\phi}{dt} = \alpha\beta Ł\frac{d\phi}{dt}$$

$$\implies \beta = \frac{m^2\omega r^2\frac{d\phi}{dt}}{\alpha L\frac{d\phi}{dt}} = \frac{m^2\omega r^2}{\alpha L}$$

$$\implies \frac{d\phi}{dt} = \frac{1}{\alpha\beta(\tau)} = \frac{1}{\alpha sin(2\tau)(1+\frac{1}{\alpha^2})+1}$$

And we can use this to solve for the function $\phi(t)$.

1.4 2-D Quantum Harmonic Oscillator

Once more defining our 2-D harmonic oscillator:

$$V(x,y) = \frac{1}{2}kx^2 + \frac{1}{2}ky^2 = \frac{1}{2}k(x^2+y^2) = \frac{1}{2}kr^2$$

We will define $k = m\omega^2$ just as before. From our potential energy we can also define a field of the force:

$$\vec{F} = -\vec{\nabla}V = -kx\hat{x} - ky\hat{y} = -kr\hat{r}$$

Now, we will write the wave equation using this established set-up:

$$\frac{-\hbar^2}{2m}\left[\frac{\partial^2\phi(x,y)}{\partial x^2} + \frac{\partial^2\phi(x,y)}{dy^2}\right] + \frac{1}{2}m\omega^2(x^2+y^2)\phi(x,y) = E\phi(x,y)$$

To convert to natural units of the problem we'll perform a change of variable where:

$$y = bu$$
$$x = bv$$

We will also have to convert the wave function to be in these new units:

$$\phi(bu, bv) \to \chi(u,v)$$

With all these changes our wave equation becomes:

$$\frac{-\hbar^2}{2mb^2}\left[\frac{\partial^2\chi(u,v)}{\partial u^2} + \frac{\partial^2\chi(u,v)}{dv^2}\right] + \frac{1}{2}m\omega^2b^2(u^2+v^2)\chi(u,v) = E\chi(u,v)$$

To define our natural units we choose $b^2 = \frac{\hbar}{m\omega}$. Additionally, energy is proportional to $\hbar\omega$, thus we can change to natural energy units where $\alpha = \frac{E}{\hbar\omega}$. Once more rewriting the wave equation:

$$\frac{\cancel{\hbar\omega}}{2}\left[\frac{\partial^2\chi(u,v)}{\partial u^2} + \frac{\partial^2\chi(u,v)}{dv^2}\right] + \frac{\cancel{\hbar\omega}}{2}(u^2+v^2)\chi(u,v) = \alpha\cancel{\hbar\omega}\chi(u,v)$$

$$\implies \frac{-1}{2}\left[\frac{\partial^2\chi(u,v)}{\partial u^2} + \frac{\partial^2\chi(u,v)}{dv^2}\right] + \frac{1}{2}(u^2+v^2)\chi = \alpha\chi$$

$$\implies \left[\frac{-1}{2}\frac{\partial^2\chi}{\partial u^2} + \frac{1}{2}u^2\chi\right] + \left[\frac{-1}{2}\frac{\partial^2\chi}{\partial v^2} + \frac{1}{2}v^2\chi\right] = \alpha\chi$$

We will assume that this wave function is separable in this way even though this is not always true, but we will operate under this assumption and then prove it later:

$$\chi(u,v) = \chi_1(u)\chi_2(v)$$

Based on this assumption we thus know that:

$$\frac{\partial\chi}{\partial u} = \left(\frac{\partial\chi_1}{\partial u}\right)\chi_2$$
$$\frac{\partial\chi}{\partial v} = \left(\frac{\partial\chi_2}{\partial v}\right)\chi_1$$

$$\frac{\partial^2 \chi}{\partial u^2} = \left(\frac{\partial^2 \chi_1}{\partial u^2}\right) \chi_2$$
$$\frac{\partial^2 \chi}{\partial v^2} = \left(\frac{\partial^2 \chi_2}{\partial v^2}\right) \chi_1$$

What this means is that we can rewrite the wave equation in the following way;

$$\frac{1}{\chi_1 \chi_2}\left[\left[\frac{-1}{2}\frac{d^2\chi_1}{du^2} + \frac{1}{2}u^2\chi_1\right]\chi_2 + \left[\frac{-1}{2}\frac{d^2\chi_2}{dv^2} + \frac{1}{2}v^2\chi_2\right]\chi_1\right] = \alpha$$

Now we can separate this into two terms where one involves only u and χ_1 and one involves only v and χ_2:

$$\frac{1}{\chi_1}\left[\frac{-1}{2}\frac{d^2\chi_1}{du^2} + \frac{1}{2}u^2\chi_1\right] + \frac{1}{\chi_2}\left[\frac{-1}{2}\frac{d^2\chi_2}{dv^2} + \frac{1}{2}v^2\chi_2\right] = \alpha$$

Therefore, this problem in essence simplifies into two separate problems:

$$\implies \frac{1}{\chi_1}\left[\frac{-1}{2}\frac{\partial^2\chi_1}{du^2} + u^2\chi_1\right] = \alpha_1$$
$$\implies \frac{1}{\chi_2}\left[\frac{-1}{2}\frac{\partial^2\chi_2}{dv^2} + v^2\chi_1\right] = \alpha_2$$

We can solve these two above just as we solved for the 1-D harmonic Oscillator

$$\alpha = \alpha_1 + \alpha_2$$
$$\implies \int_{-\infty}^{\infty} du \int_{-\infty}^{\infty} dv \ \chi_1^2(u)\chi_2^2(v) = 1$$
$$= \left[\int_{-\infty}^{\infty} du \chi_1^2(u)\right]\left[\int_{-\infty}^{\infty} dv \chi_2^2(V)\right] = 1$$

(If each of the integrals in the bracket is 1, the total is also 1)

Using the same logic and math as in the 1-D Harmonic Oscillator, the solutions would thus look like this:

$$\alpha_1 = n_1 + \frac{1}{2}, \qquad n_1 = 0, 1, 2, ...$$
$$\alpha_2 = n_2 + \frac{1}{2}, \qquad n_2 = 0, 1, 2, ...$$
$$\alpha = \alpha_1 + \alpha_2 = 1 + n_1 + n_2$$

The energy levels for the 2-D Harmonic Oscillator would thus look like this:

$$n_1 \qquad n_2 \qquad \alpha$$

0	0	1
1	0	2
0	1	2
1	1	3
2	0	3
0	2	3
2	1	4
1	2	4
3	0	4
0	3	4

****

Side Note: Using the same idea, the energy levels for 3-D Harmonic Oscillator would be:

$$\alpha = \alpha_1 + \alpha_2 + \alpha_3 = \frac{3}{2} + n_1 + n_2 + n_3$$

n_1	n_2	n_3	α
0	0	0	$\frac{3}{2}$
1	0	0	$\frac{5}{2}$
0	1	0	$\frac{5}{2}$
0	0	1	$\frac{5}{2}$
1	1	0	$\frac{7}{2}$
0	1	1	$\frac{7}{2}$
1	0	1	$\frac{7}{2}$
2	0	0	$\frac{7}{2}$
0	2	0	$\frac{7}{2}$
0	0	2	$\frac{7}{2}$

This demonstrates how degeneracy increases the more dimensions you go into. Heat will also affect the particle or object less because there are more energy states than can be occupied at lower energies before reaching higher ones. In other words, "If you want to be cool go to higher dimensions!"

****

Now let's look at the solutions for these separated wave functions χ_1 and χ_2 when we change the energy level in a given dimension. As we might recall from the 1-D harmonic oscillator solution, the two lowest Hermite polynomials are $H_0 = 1$ and $H_1(y) = \sqrt{2}y$

$\underline{n_1 = 0}$

$$\chi_1(u) = \frac{1}{\sqrt{2\pi}} e^{\frac{-u^2}{2}}$$

$\underline{n_2 = 0}$

$$\chi_2(v) = \frac{1}{\sqrt{2\pi}} e^{\frac{-v^2}{2}}$$

$\underline{n_1 = 1}$

$$\chi_1(u) = \frac{1}{\sqrt{2\pi}} (\sqrt{2}u) e^{\frac{-u^2}{2}}$$

$\underline{n_2 = 1}$

$$\chi_2(v) = \frac{1}{\sqrt{2\pi}} (\sqrt{2}v) e^{\frac{-v^2}{2}}$$

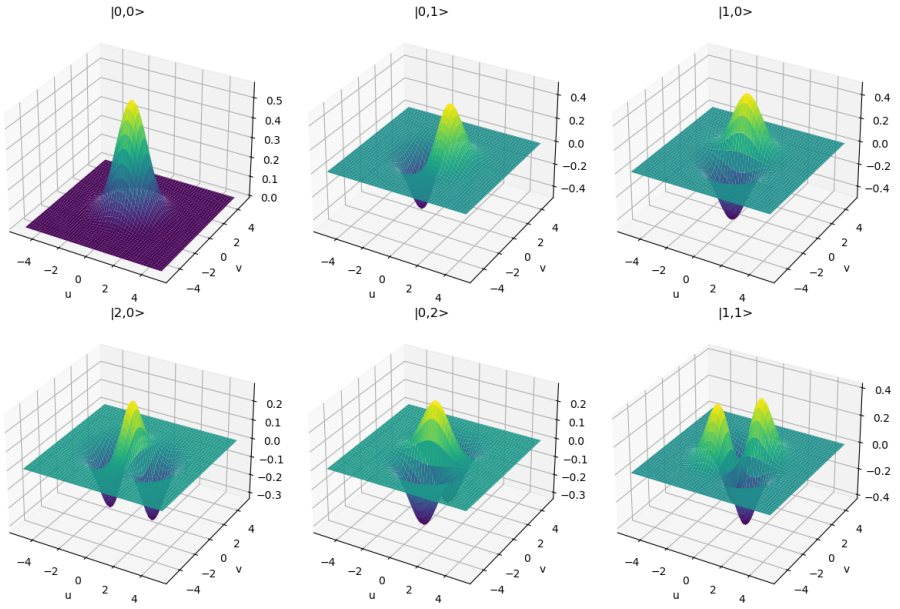
We could continue this pattern using the same relationship derived for the 1-D harmonic oscillator:

$$H_{n+1}(y) = \frac{1}{\sqrt{2(n+1)}} \left[-\frac{dH_n(y)}{dy} + 2yH_n(y) \right]$$

Now, combining these separate n_1 and n_2 values leads to many degenerate states (wave functions for each value of n. Looking back at our table of states and including the wave function now:

n_1	n_2	α	χ
0	0	1	$\frac{1}{2\pi} e^{\frac{-r^2}{2}}$
1	0	2	$\frac{1}{2\pi} \sqrt{2} r sin\theta e^{\frac{-r^2}{2}}$
0	1	2	$\frac{1}{2\pi} \sqrt{2} r cos\theta e^{\frac{-r^2}{2}}$
1	1	3	$\frac{2uv}{\sqrt{\pi}} e^{\frac{-r^2}{2}}$
2	0	3	$\frac{1}{2\pi^2} r^2 sin^2\theta e^{-r^2}$
0	2	3	$\frac{1}{2\pi^2} r^2 cos^2\theta e^{-r^2}$

These graphs can then be plotted, demonstrating the radial symmetry of some solutions and not others.



Let's now try to understand the 2-D harmonic oscillator in the language of eigenvectors and eigenvalues. We are already familiar with the operator H that extracts the energy of the wave function/eigenvector. But how about an operator that allows us to find eigenvectors of higher energy states? And how about finding higher energy states in both the u direction and the v direction?

Well, since we already showed how the 2D harmonic oscillator in essence simplifies into two 1D problems, it may not be surprising that the operators work in the same way, and are as follows:

$$a_u = \frac{1}{\sqrt{2}}\left[\frac{\partial}{\partial u} + u\right]$$

$$a_v = \frac{1}{\sqrt{2}}\left[\frac{\partial}{\partial v} + v\right]$$

$$a_u^\dagger = \frac{1}{\sqrt{2}}\left[\frac{-\partial}{\partial u} + u\right]$$

$$a_v^\dagger = \frac{1}{\sqrt{2}}\left[\frac{-\partial}{\partial v} + v\right]$$

By looking at these operators we know that similar to the 1D operators:

$$\left[a_u, a_u^\dagger\right] = 1$$

$$\left[a_v, a_v^\dagger\right] = 1$$

Any other commutators between u operators and v operators are zero, so in this way also the problem splits into two separate problems:

$$[a_u, a_v] = 0$$
$$\left[a_u, a_v^\dagger\right] = 0$$
$$\left[a_u^\dagger, a_v\right] = 0$$
$$\left[a_u^\dagger, a_v^\dagger\right] = 0$$

Just like in the 1-D harmonic oscillaotr, we will also define N operators for each dimension:

$$N_u = a_u^\dagger a_u$$
$$N_v = a_v^\dagger a_v$$

And again like the 1-D harmonic oscillator, we can prove the following in the same exact way:

$$[N_u, a_u] = -a_u$$
$$\left[N_u, a_u^\dagger\right] = a_u^\dagger$$

$$[N_v, a_v] = -a_v$$
$$\left[N_v, a_v^\dagger\right] = a_v^\dagger$$

And once more, when we try to find the commutators for crossed operators between u and v, the result is zero. For example:

$$[N_u, a_v] = 0$$
$$\left[N_v^\dagger, a_u\right] = 0$$
$$...$$

The total wave equation is thus:

$$(N_u + N_v)\chi = (\alpha - 1)\chi$$

Now, (just like in the 1-D H.O.!!) we will use our operators $a_u, a_v, a_u^\dagger, a_v^\dagger$ to uncover all the different energy states. Applying $a_u^\dagger$:

$$(N_u + N_v)(a_u^\dagger \chi) = \left[a_u^\dagger N_u + a_u^\dagger\right]\chi = a_u^\dagger(\alpha - 1 + 1)\chi = \alpha(a_u^\dagger \chi)$$

$$(N_u + N_v)(a_u^\dagger \chi) = \alpha(a_u^\dagger \chi)$$

Therefore the energy of this new eigenvector $a_u^\dagger \chi$ is α compared to the energy of χ which was $\alpha - 1$. The operator $a_u^\dagger$ thus changes from one eigenvector to a

higher energy one. The same is true for $a_v^\dagger$, the only difference being that the energy of the state is increased in a different dimension.

To discover a lower energy state, we can apply either a_u or a_v. For example:

$$(N_u + N_v)(a_v\chi) = (\alpha - 1 - 1)(a_u\chi)$$

So with these operators we can uncover all the different energy eigenvectors.

In order to not have eigenvectors with negative eigenvalues (just like in 1D H.O.!!) we know that there must be some χ_{00} where:

$$(a_u^\dagger a_+ a_v^\dagger a_v)\chi_{00}(u,v) = 0$$

$$a_u\chi_{00}(u,v) = 0 \ \textit{and} \ a_v\chi_{00}(u,v) = 0$$

Let's find this χ_{00}:

$$\left(\frac{\partial}{\partial u} + u\right)\chi_{00} = 0$$

$$\implies \chi_{00}\left[\frac{\partial ln\chi_{00}}{\partial u} + u\right] = 0 \implies \chi_{00}\frac{\partial}{\partial u}\left[ln\chi_{00} + \frac{1}{2}u^2\right] = 0$$

This implies that $ln\chi_{00} + \frac{1}{2}u^2$ is a function of v which we will call $f(v)$, meaning $ln\chi_{00} = f(v) - \frac{1}{2}u^2$. We will substitute this below:

$$\left(\frac{\partial}{\partial v} + v\right)\chi_{00} = 0 \implies \chi_{00}\frac{\partial}{\partial v}\left[ln\chi_{00} + \frac{1}{2}v^2\right] = 0$$

$$\implies \chi_{00}\frac{\partial}{\partial v}\left[f(v) - \frac{1}{2}u^2 + \frac{1}{2}v^2\right] = 0$$

$$\implies \frac{\partial}{\partial v}\left[f(v) + \frac{1}{2}v^2\right] = 0$$

Finally we end up with a solution for the lowest energy wave function:

$$ln\chi_{00} + \frac{1}{2}u^2 + \frac{1}{2}v^2 = \textit{constant}$$

$$\implies \chi_{00} = \frac{1}{\sqrt{\pi}}e^{-\frac{1}{2}(u^2+v^2)}$$

From this lowest energy state what we end up with is branches in each of the two dimensions for moving to a higher energy state using these operators:

So, let's try to find some of these wave functions. Starting with χ_{10}:

$\underline{\alpha = 1:}$

$$n_{10}\,\chi_{10} = a_u^\dagger\chi_{00} = \frac{1}{\sqrt{2\pi}}\left[2ue^{\frac{-(u^2+v^2)}{2}}\right] = \sqrt{\frac{2}{\pi}}ue^{\frac{-(u^2+v^2)}{2}}$$

In this equation n_{10} is the normalization constant for χ_{10} which we can solve for as follows:

$$n_{10}^2 = \frac{2}{\pi}\int_{-\infty}^{\infty} du \int_{-\infty}^{\infty} dv u^2 e^{-(u^2+v^2)}$$

We set $u = rsin\theta$ and $v = rcos\theta$ and then solve:

$$n_{10}^2 = \frac{2}{\pi}\int_0^{\infty} rdr \int_0^{2\pi} d\theta r^2 sin^2\theta e^{-r} = \frac{1}{\pi}\left[\int_0^{\infty} r^3 e^{-r^2} dr\right]\left[\int_0^{2\pi}(2sin^2\theta)d\theta\right]$$

$$= \frac{1}{\pi}\frac{1}{2}2\pi = 1$$

$$\implies n_{10}^* n_{10} = 1$$

Therefore, if we repeat the process for χ_{01} we would find that the constant is the same, 1. This also makes sense in that our decision to decide $u = rsin\theta$ and $v = rcos\theta$ is arbitrary and we could have easily done vice versa. The final result for these two is thus:

$$\chi_{10} = \sqrt{\frac{2}{\pi}} u e^{\frac{-(u^2+v^2)}{2}}$$

$$\chi_{01} = \sqrt{\frac{2}{\pi}} v e^{\frac{-(u^2+v^2)}{2}}$$

Experimentalist's Perspective

We have been so far talking about discrete quantum states, but an experimentalist's quantum states may be linear combinations of what we have.

So, an experimentalist will see a linear combination and measure the energy such as:

$$H(c_1\chi_{10} + c_2\chi_{01}) = c_1(H\chi 0, 0) + c_2(H\chi_{1,0})$$

This means that $c_1\chi_{0,0} + 2c_2\chi_{1,0}$ is not proportional to $c_1\chi_{0,0} + c_2\chi_{1,0}$ which means that the sum of two eigenvectors does not give you another eigenvector!

In order to solve for what the experimentalist really measured we first can normalize like this:

$$\int_{-\infty}^{\infty} [(c_1\chi_{1,0} + c_2\chi_{0,1})(c_1\chi_{1,0} + c_2\chi_{0,1})]\, dudv = 1$$

$$\implies c_1^2 + c_2^2 = 1 \implies c_1 = \sqrt{1 - c_1^2}$$

We will use this relationship between coefficients to solve later. First though let's look back at a proof from earlier:

$$H\chi_1 = \alpha_1\chi_1 \implies \chi_1^\dagger H = \alpha_1\chi_1^\dagger$$
$$H\chi_2 = \alpha_2\chi_2 \implies \chi_2^\dagger H = \alpha_2\chi_2^\dagger$$
$$\chi_1^\dagger H\chi_2 = \alpha_1\chi_1^\dagger\chi_2 = \alpha_2\chi_1^\dagger\chi_2 \implies (\alpha_1 - \alpha_2)(\chi_1^\dagger\chi_2) = 0$$
$$\chi_2^\dagger H\chi_1 = \alpha_2\chi_2^\dagger\chi_1 = \alpha_1\chi_2^\dagger\chi_1 \implies (\alpha_1 - \alpha_2)(\chi_2^\dagger\chi_1) = 0$$

If $\alpha_1 \neq \alpha_2$, then in order for this to be 0, $\chi_1^\dagger\chi_2 = 0$
Now let's assume the experimentalist knows the coefficients:

$$\frac{2}{\pi}[c_1^2u^2 + 2c_1c_2uv + c_2v^2]e^{-(u^2+v^2)}$$

$$\implies \frac{2}{\pi}[c_1^2sin^2\theta + 2c_1c_2sin\theta cos\theta + c_2^2cos^2\theta]r^2e^{-r^2}$$

$$= \frac{2}{\pi}\left[\frac{1}{2} + \frac{c_1 + c_2}{2}cos2\theta + c_1c_2sin2\theta\right]$$

From here the experimentalists can use "partial wave decomposition" to find the coefficients of each of the terms. Different combinations of the coefficients will lead to different types of waves.

Now we will Solve this problem once more but in polar coordinates!

This is the change of variables we will make:

$$u = cos\theta$$
$$v = rsin\theta$$

$$du = drcos\theta - rsin\theta d\theta$$
$$dv = drsin\theta + rcos\theta d\theta$$

$$\implies dr = ducos\theta + dvsin\theta$$
$$\implies d\theta = \frac{-dusin\theta}{r} + \frac{dvcos\theta}{r}$$

Now we want to change the entire wave equation to be in terms of θ and r and their partial derivatives. So, we'll start by taking the partial derivatives of each of these:

$$\left.\frac{\partial}{\partial u}\right|_v \begin{bmatrix}\chi_{(U,V)}\\ \chi_{(r,\theta)}\end{bmatrix} = \left(\left.\frac{\partial}{\partial\theta}\right|_r \left.\frac{\partial\theta}{\partial U}\right|_v + \left.\frac{\partial}{\partial r}\right|_\theta \left.\frac{\partial r}{\partial U}\right|_v\right)\chi(r,\theta)$$
$$= \left[-\frac{sin\theta}{r}\frac{\partial}{\partial\theta} + cos\theta\frac{\partial}{\partial r}\right]\chi(r,\theta)$$

$$\frac{\partial}{\partial v} = \Big|_u [\chi_{(r,\theta)}] = \left(\frac{\partial}{\partial \theta}\Big|_r \frac{\partial \theta}{\partial v}\Big|_u + \frac{\partial}{\partial r}\Big|_\theta \frac{\partial r}{\partial V}\Big|_u \right) \chi(r,\theta)$$
$$= \left[\frac{cos\theta}{r} \frac{\partial}{\partial \theta} + sin\theta \frac{\partial}{\partial r} \right] \chi_{(r,\theta)}$$

Then we can take the second partial derivatives and sum the two together, notice that many of the terms cancel out, and then end up with the wave function:

$$\left(\frac{\partial^2}{\partial U^2} + \frac{\partial^2}{\partial V^2} \right) \chi_{(r,\theta)} = \frac{1}{r^2} \frac{\partial^2 \chi}{\partial \theta^2} + \frac{1}{r} \frac{\partial \chi}{\partial r} + \frac{\partial^2 \chi}{\partial r^2}$$

This means that the Hamiltonian operator thus becomes:

$$H = -\frac{1}{2} \left(\frac{\partial^2}{\partial r^2} + \frac{1}{r} \frac{\partial}{\partial r} + \frac{1}{r^2} \frac{\partial^2}{\partial \theta^2} \right) + \frac{1}{2} r^2$$

Looking at this new Hamiltonian operator, we can presume that the first two terms are probably linear kinetic terms (they only derive with respect to r thus depend on r), the third term is probably angular kinetic energy, and the last is our potential energy.

We define the operator $L_z = \frac{\partial}{\partial \theta}$ and thus the Hamiltonian can be rearranged:

$$H = -\frac{1}{2} \left(\frac{\partial^2}{\partial r^2} + \frac{1}{r} \frac{\partial}{\partial r} + \frac{1}{r^2} L_z^2 - r^2 \right)$$

Now, let's check that this new operator we defined commutes with the Hamiltonian:

$$(HL_z)\chi = -\frac{1}{2} \left[\frac{\partial^2}{\partial r^2} + \frac{1}{r} \frac{d^2}{d\theta^2} - r^2 \right] \left[\frac{d\chi}{d\theta} \right]$$

$$(L_z H)\chi = -\frac{1}{2} \frac{\partial}{\partial \theta} \left[\frac{\partial^2 \chi}{\partial r^2} + \frac{1}{r} \frac{\partial \chi}{\partial r} + \frac{1}{r^2} \frac{\partial^2 \chi}{\partial \theta^2} - r^2 \chi \right]$$

These two are the same so we know that:

$$(HL_z - L_z H)\chi = 0 = [H, L_z]$$

If χ is an eigenvector with eigenvalue α, then $L_z\chi$ is also an eigenvector with an eigenvalue α. This means L_z can help with finding degenerate states. So, states will need to be defined in terms of the H and L_z exam.

We want to find these degenerate states through:

$$L\chi(r,\theta) = \frac{\partial}{\partial \theta} \chi(r,\theta)$$

We know that θ and $\theta + 2\pi$ must label the same point so we need a function such that $f(\theta) = f(\theta + 2\pi)$. The functions $cos(n\theta)$ and $sin(n\theta)$ do not work because the are not valid eigenvectors. So instead we will use:

$$e^{in\theta} = cos(n\theta) + isin(\theta)$$
$$e^{-in\theta} = cos(n\theta) - isin(\theta)$$

Instead of calling this integer n we will instead call it m, using the operator:

$$\frac{\partial}{\partial\theta}(e^{im\theta}) = ime^{im\theta}$$

Therefore the result of the operator, which we were previously just calling l, is im. Furthermore we might have some function that does not depend on θ such that:

$$\chi(r,\theta) = R(r)e^{im\theta}$$

Now we have fixed energy and angular momentum, just like in classical mechanics but instead it is now like:

$$H\chi = \chi\chi$$
$$L_z\chi = im\chi$$

**Note: it can be useful to instead define $L_z = i\frac{\partial}{\partial\theta}$ so that it is hermitian and we get values of m instead of im but we're not doing that.

Therefore H becomes:

$$H = \frac{1}{2}\left(\frac{d^2}{dr^2} + \frac{1}{r}\frac{d}{dr} - \frac{m^2}{r^2} - r^2\right)$$

The wave function thus becomes $HR = \alpha R$ where R is some function that depends on r.

We can therefore rewrite the wave equation:

$$\left[\frac{d^2}{dr^2} + \frac{1}{r}\frac{d}{dr} - \frac{m^2}{r^2} - r^2 + 2\alpha\right]R(r) = 0$$

This R function can be written as:

$$R(r) = P(r)e^{-\frac{r^2}{2}}$$

Now let's rewrite the wave equation in these terms and it becomes:

$$\frac{d^2P}{dr^2} + \left(\frac{1}{r} - 2r\right)\frac{dP}{dr} + \left(2\alpha - 2 - \frac{m^2}{r^2}\right)P = 0$$

Also with this new definition of R, the wave function becomes:

$$\chi(r,\theta) = R(r)P(r)e^{\frac{-r^2}{2}}e^{im\theta}$$

We can normalize this wave function as follows:

$$\int_0^\infty r dr \int_0^{2\pi} d\theta \chi^*(r,\theta)\chi(r,\theta) = 1$$

In order to perform this normalization, we require $P(r)$ to be a finite polynomial.

So let's assume $P(r) = r^\beta$ for $r \to 0$, then $\frac{dP}{dr} = \beta r^{\beta-1}$

Plugging this into the wave function our end result will be:

$$[\beta(\beta-1) + \beta - m^2]r^{\beta-2} + [2\alpha - 2 - 2\beta]r^\beta = 0$$

Since both of these terms are positive real values, then examining the first term:

$$\beta(\beta-1) + \beta - m^2 = 0 \implies \beta^2 = m^2$$
$$\implies \beta = |m|$$

So, β, which is the power of $P(r)$, is the same as the absolute value of m, where im is our eigenvalue of the operator L.

However, we only approximated that $P(r) = r^\beta$. In reality, an accurate way to represent it may be that $P(r) = r^{|m|}U(r)$ where U is another polynomial.

Once more we can substitute this into our wave equation in terms of P and manipulate to obtain:

$$0 = (m^2 - |m| + |m| - m^2)r^{|m|-2}U(r) + (2\alpha - 2 - 2|m|)r^{|m|}U(r) + [(2|m|+1)r^{|m|+1} - 2r^{|m|+1}] + r^{|m|}\frac{d^2U}{dr^2}$$

$$\implies \frac{d^2U}{dr^2} + (\frac{2|m|+1}{r} - 2r)\frac{dU}{dr} + 2(\alpha - 1 - |m|)U = 0$$

Now, let's consider this U(r) as a sum:

$$\sum_{n=1}^{\infty} U_n r^n$$

With this in my mind, we can manipulate and rewrite our wave equation one more to end up with:

$$0 = \frac{2|m|+1}{2}U_1 + \sum_{n=0}^{\infty}[U_{n+2}[(n+2)(n+1) + (2|m|+1)(n+2)] + U_n(2(\alpha - 1 - |m|) - 2n)]r^n$$

Now we know that in order for this expression to equal 0 at any r that all the coefficients of every term must be 0:

$$U_1 = 0$$
$$U_{n+2}[(n+2)(n+1) + (2|m|+1)(n+2)] + U_n(2(\alpha - 1 - |m|) - 2n) = 0$$

$$\implies U_{n+2} = \frac{2[1 + |m| + n - \alpha]}{(n+2)(2|m| + n + 2)} U_n$$

For some N, we thus know that $U_N = 0$, meaning that:

$$1 + |m| + N - \alpha = 0$$

$$\implies \alpha = N + 1 + |m|$$

This is our restriction on α and shows that only some values of α are allowed.

Final note, when it comes to finding solely linear or rotational kinetic energy or potential energy, this can be done through integrating the wave function as follows and since it separates into multiple integrals, each part of the total energy can be solved for separately, like so:

$$\int \chi^*(-\frac{1}{2}(\frac{\partial^2}{\partial r^2} + \frac{1}{r}\frac{\partial}{\partial r})\chi + \int \chi^*[-\frac{1}{2}\frac{1}{r_2}\frac{\partial^2}{\partial r^2}]\chi + \int \chi^* \left[\frac{1}{2}r^2\right]\chi$$

In this integral the first term is linear kinetic energy, second term is rotational kinetic energy, and third term is potential energy.

Quantum Mechanics- Part 5

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Contents

1 Understanding and Defining an Angular Momentum Operator in Cartesian Coordinates

1.1 Centered Potentials

In quantum mechanics there are various models of potentials that are used such as the following:

$$V(r) = \frac{1}{2}kr^2 \text{ (spring)} \tag{1}$$

$$V(r) = \frac{\alpha}{r}, \alpha > 0 \text{ (electric)} \tag{2}$$

$$V(r) = Kr \text{ (confining)} \tag{3}$$

$$V(r)\frac{\alpha}{r}e^{-mr} \text{ (Higgs)} \tag{4}$$

$$\begin{gathered} V(r) = \text{"Evolving" nuclear potential} \\ \text{such as Reid potential or Cornell potential} \end{gathered} \tag{5}$$

Based on one of these potentials that are proportional to radius, it is useful to define an angular momentum operator in each of our directions in Cartesian coordinates.:

$$\vec{L} = \vec{r} \times \vec{p} \tag{6}$$

$$L_x = yp_z - zp_y = -i\hbar\left[y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right] \tag{7}$$

$$L_y = zp_x - xp_z = -i\hbar\left[z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right] \tag{8}$$

$$L_z = xp_y - yp_x = -i\hbar\left[x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right] \tag{9}$$

Likewise, we recall that for wave functions of the form we use, the momentum operators are:

$$p_x = -i\hbar\frac{\partial}{\partial x} \tag{10}$$

$$p_y = -i\hbar\frac{\partial}{\partial y} \tag{11}$$

$$p_z = -i\hbar\frac{\partial}{\partial z} \tag{12}$$

1.2 Commuting Angular Momentum Projection Operators

Let's understand better by seeing whether these angular momentum operators commute with each other. Let's first try $[L_x, L_y]$:

$$\begin{aligned}(L_xL_y)\psi &= -\hbar^2\left[y\frac{\partial}{\partial z} - z\frac{\partial}{\partial z}\right]\left[z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right]\psi = -\hbar^2\left[y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right]\left[z\frac{d\psi}{dx} - x\frac{d\psi}{dz}\right] \\ &= -\hbar^2\left[y\frac{\partial z}{\partial z}\frac{\partial\psi}{\partial x} + yz\frac{\cancel{\partial^2\psi}}{\cancel{\partial z}\partial x} - z^2\frac{\cancel{\partial^2\psi}}{\cancel{\partial y}\partial x} - yx\frac{\cancel{\partial^2\psi}}{\cancel{\partial z^2}} + zx\frac{\cancel{\partial^2\psi}}{\cancel{\partial y}\partial z}\right] \\ &= -\hbar^2 y\frac{\partial\psi}{\partial x}\end{aligned} \tag{13}$$

$$\begin{aligned}(L_yL_x)\psi &= -\hbar^2\left[z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right]\left[y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right]\psi = -\hbar^2\left[z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right]\left[y\frac{\partial\psi}{\partial z} - z\frac{\partial\psi}{\partial y}\right] \\ &= -\hbar^2\left[zy\frac{\cancel{\partial^2\psi}}{\cancel{\partial x}\partial z} - xy\frac{\cancel{\partial^2\psi}}{\partial^2 z^2} - z^2\frac{\partial^2\psi}{\cancel{\partial x}\partial y} + x\frac{\cancel{\partial z}}{\partial z}\frac{\partial\psi}{\cancel{\partial y}} + xz\frac{\cancel{\partial^2\psi}}{\cancel{\partial z}\partial y}\right] \\ &= -\hbar^2 x\frac{\partial\psi}{y}\end{aligned} \tag{14}$$

The commutator is thus:

$$\begin{aligned}(L_xL_y - L_yL_x)\psi &= -\hbar^2\left[x\frac{\partial\psi}{\partial y} - y\frac{\partial\psi}{\partial x}\right] = (i\hbar)(-i\hbar)\left[x\frac{\partial\psi}{\partial y} - y\frac{\partial\psi}{\partial x}\right] \\ &= i\hbar L_z\psi\end{aligned} \tag{15}$$

$$[L_x, L_y] = i\hbar L_z \tag{16}$$

So these operators <u>do not</u> commute!
Now let's try $[L_y, L_z]$:

$$\begin{aligned}(L_yL_z - L_zL_y) &= \{\left[z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right]\left[x\frac{\partial}{\partial y}\right] - y\left[\frac{\partial}{\partial x}\right] - \left[x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right]\left[z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right]\} \\ &= -\hbar^2\{z\frac{\partial}{\partial y} - y\frac{\partial}{\partial z}\} = (i\hbar)(-i\hbar)\left[z\frac{\partial}{\partial z} - z\frac{\partial}{\partial x}\right] = i\hbar L_y\end{aligned} \tag{17}$$

These don't commute either!
The results of all three combinations is:

$$[L_x, L_y] = i\hbar L_z \tag{18}$$

$$[L_y, L_z] = i\hbar L_x \tag{19}$$

$$[L_z, L_x] = i\hbar L_y \tag{20}$$

This can be summarized as:

$$[L_i, L_j] = i\hbar \mathcal{E}_{ijk} \tag{21}$$

where:

$$\mathcal{E}_{ijk} = \begin{cases} 0, & \text{if } i = j \text{ or } j = k \text{ or } i = k \\ 1, & \text{if odd permutation (such as } i = 1, j = 2, k = 3) \\ -1, & \text{if even permutation} \end{cases} \tag{22}$$

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Side note: This $\mathcal{E}_{ijk}$ is used in the definition of the cross product

$$\vec{A} \times \vec{B} = \vec{C} \tag{23}$$

$$\mathcal{E}_{ijk} A_j B_k = C_i \tag{24}$$

Other examples of its use:

1) Volume differential

$$(dy\hat{y}) \times (dz\hat{z}) = (dydz)\hat{x} \tag{25}$$

$$(dx\hat{x}) \cdot [(dy\hat{y}) \times (dz\hat{z})] = dxdydz \tag{26}$$

$$\frac{1}{6}[\mathcal{E}_{ijk} d\hat{x}_i d\hat{x}_j d\hat{x}_k] \tag{27}$$

2) Determinant

$$\mathcal{E}_{i_1 i_2} A_{1 i_1} A_{2 i_1} = det A_{2\times 2} \tag{28}$$

$$\mathcal{E}_{i_1 i_2 i_3} A_{1 i_1} A_{2 i_1} A_{3 i_3} = det A_{3\times 3} \tag{29}$$

$$\mathcal{E}_{i_1 i_2 i_3 \ldots i_n} A_{1 i_1} A_{2 i_1} A_{3 i_3} \ldots A_{n i_n} = det A_{n\times n} \tag{30}$$

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Note 2: Here are some useful commutator proofs for upcoming math we will do in this chapter:

$$\begin{aligned}[A, BC] = ABC - BCA = ABC - BAC - BCA + BAC \\ = [A, B]C + B[A, C]\end{aligned} \tag{31}$$

$$[A + B, C] = [A, C] + [B, C] \tag{32}$$

$$[AB, C] = ABC - CAB - ACB + ACB = A[B, C] + [A, C]B \tag{33}$$

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1.3 Commuting Total Angular Momentum Operator

If L_x, L_y, L_z yield the projections of the angular momentum in x, y, z directions, then the total angular momentum operator L is understood through $L^2 = L_x^2 + L_y^2 + L_z^2$

So, does L_x commute with L_x^2?

$$[L_x, L_x^2] = L_x L_x^2 - L_x^2 L_x = L_x^3 - L_x^3 = 0 \tag{34}$$

Yes.

Does L_x commute with L_y^2? To figure this out we use the property defined in (31) and the commutator (18).

$$[L_x, L_y^2] = [L_x, L_y]L_y + L_y[L_x, L_y] = i\hbar(L_z L_y + L_y L_z) \tag{35}$$

No, and we will use this information to understand how the total angular momentum commutes

Similarly, using (20):

$$[L_x, L_z^2] = -i\hbar(L_y L_z + L_z L_y) \tag{36}$$

With this information we can see if L_x commutes with the total angular momentum squared L^2 where, as we said $L^2 = L_x^2 + L_y^2 + L_z^2$ so we just sum the separate commutators (32) to find:

$$[L_x, L_x^2 + L_y^2 + L_z^2] = 0 \tag{37}$$

We can do the same process for L_y to find that it also commutes with the total angular momentum:

$$[L_y, L^2] = [L_y, L_x]L_x + L_x[L_y, L_x] + [L_y, L_z]L_z + L_z[L_y, L_z] = i\hbar(L_{xz} - L_{zx}) = 0 \tag{38}$$

In conclusion:

$$[L_x, L^2] = 0 \tag{39}$$

$$[L_y, L^2] = 0 \tag{40}$$

$$[L_z, L^2] = 0 \tag{41}$$

1.4 Simultaneously diagonalizing (finding a solution set) total angular momentum operator and its projection in one direction.

We want to simultaneously diagonalize one angular momentum projection operator and the total angular momentum operator but in order to do that we'll first show that it is even possible.

We define the effect of these two operators on a ket/wave function and the eigenvalues they extract as follows:

$$L^2 \left|l, m\right\rangle = l^2 \left|l, m\right\rangle \tag{42}$$

$$L_z \left|l.m\right\rangle = m \left|l, m\right\rangle \tag{43}$$

The commutator of the total angular momentum squared and one of the projections is as follows:

$$\begin{aligned}
[L^2, L_c] = \left[\sum_{a=1}^{3} L_a^2, L_c\right] = \sum_{a=1}^{3} [L_a L_a, L_c] = \sum_{a=1}^{3} \{L_a[L_a, L_c] + [L_a, L_c]L_a\} \\
= \sum_{a=1}^{3} \left\{ L_a i\hbar \sum_{b=1}^{3} \mathcal{E}_{acb} L_b + i\hbar \sum_{b=1}^{3} \mathcal{E}_{acb} L_b \right\} = i\hbar \sum_{a,b=1}^{3} \{\mathcal{E}_{acb} L_a L_b + \mathcal{E}_{acb} L_b L_a\} \\
= i\hbar \sum_{a,b=1}^{3} \mathcal{E}_{acb} L_a L_b + \sum_{a,b=1}^{3} \mathcal{E}_{acb} L_b L_a = i\hbar \sum_{a,b=1}^{3} (\mathcal{E}_{acb} + \mathcal{E}_{bca}) L_a L_b \\
= i\hbar \sum_{a,b=1}^{3} (0) L_a L_b = 0
\end{aligned} \tag{44}$$

Since we just showed that L^2 and L_c commute with each other, we can simultaneously diagonalize them. In our case, we will set $L_c = L_z$ but we could have instead chosen L_x or L_y.

Now, we want simultaneously diagonalize L^2 and L_z, let's first denote the eigenvalues of each but this time, remembering that these operators extract an $\hbar$ every time they are applied we will denote:

$$L^2 \left|l, m\right\rangle = \hbar^2 l^2 \left|l, m\right\rangle \tag{45}$$

$$L_z \left|l, m\right\rangle = \hbar m \left|l, m\right\rangle \tag{46}$$

Additionally we remember that these operators in each direction (where L_1, L_2, L_3 are in our case equivalent to L_x, L_y, L_z) are hermitian:

$$L_1^\dagger = L_1 \tag{47}$$

$$L_2^\dagger = L_2 \tag{48}$$

$$L_3^\dagger = L_3 \tag{49}$$

Now, let's use this to try to better understand these components of the angular momentum. The expectation value of L_1^2 is:

$$\langle l,m|L_1^2|l,m\rangle = \langle l,m|L_1(L_1|l,m\rangle) = (L_1\,|l,m\rangle)^\dagger(L_1\,|l,m\rangle) \geq 0 \tag{50}$$

Likewise:

$$\langle l,m|L_2^2|l,m\rangle \geq 0 \tag{51}$$

$$\langle l,m|L_3^2|l,m\rangle \geq 0 \tag{52}$$

$$\implies m^2 \geq 0 \tag{53}$$

So the squared eigenvalues of L_1^2,L_2^2, and L_3^2 will be positive, meaning they must be real. In the case of L_3, m must be real.

If we add two together we get:

$$\langle l,m|L_1^2 + L_2^2|l,m\rangle = \langle l,m|L^2 - L_3^2|l,m\rangle \geq 0 \tag{54}$$

$$\hbar^2 l^2\,\langle l,m|l,m\rangle - \hbar^2 m^2\,\langle l,m|l,m\rangle = \hbar^2 l^2 - \hbar^2 m^2 = \hbar^2(l^2-m^2) \tag{55}$$

$$\implies l^2 \geq m^2 \tag{56}$$

This means that the total angular momentum is more than or equal to its projection in a particular direction.

Now we will define some new operators that will help in diagonalizing our L^2 and L_Z operators:

$$L_+ = L_1 + iL_2 \tag{57}$$

$$L_- = L_1 - iL_2 \tag{58}$$

We can see that:

$$(L_+)^\dagger = (L_1+iL_2)^\dagger = L_1^\dagger + (iL_2)^\dagger = L_1^\dagger - iL_2^\dagger = L_1 - iL_2 = L_- \tag{59}$$

This will be helpful later.

Now let's look into how these new operators commute, first with L_3:

$$\begin{aligned}[L_3,L_+] = [L_3,L_1] + i[L_3,L_2] = i\hbar L_2 + i(-i\hbar L_1) = \hbar L_1 + i\hbar L_2 \\ = \hbar(L_1+iL_2) = \hbar L_+\end{aligned} \tag{60}$$

$$\begin{aligned}[L_3,L_-] = [L_3,L_1] - i[L_3,L_2] = i\hbar L_2 - i(-i\hbar L_1) = -\hbar L_1 + i\hbar L_2 \\ = -\hbar(L_1-iL_2) = -\hbar L_-\end{aligned} \tag{61}$$

And let's look into how they commute with each other:

$$\begin{aligned}[L_+,L_-] = [L_1+iL_2, L_1+iL_2] \\ = \cancel{[L_1,L_1]} - i[L_1,L_2] + i[L_2,L-1] + \cancel{[L_2,L_2]} = -i(i\hbar L_3) + i(i\hbar L_3) \\ = 2\hbar L_3\end{aligned} \tag{62}$$

Finally let's look into how they commute with L^2:

$$[L^2, L_+] = [L^2, L_1] + i[L^2, L_2] = 0 \tag{63}$$

$$[L^2, L_-] = 0 \tag{64}$$

Let's see what happens when we try to apply L^2 to the vector created after applying L_+, remembering that we now know that these two operators commute so we can change their order:

$$L^2(L_+ |l, m\rangle) = L_+ L^2 |l, m\rangle = \hbar^2 l^2 (L_+ |l, m\rangle) \tag{65}$$

This shows that $(L_+ |l, m\rangle)$ is also an eigenvector of L^2 with an eigenvalue of $\hbar^2 l^2$.

Similarly we can apply L_3 after applying L_+:

$$\begin{aligned} L_3(L_+ |l, m\rangle) &= (L_3 L_+) |l, m\rangle = (\hbar L_+ + L_+ L_3) |l, m\rangle \\ &= \hbar L_+ |l, m\rangle + \hbar m L_+ |l, m\rangle = \hbar(m+1)(L_+ |l, m\rangle) \end{aligned} \tag{66}$$

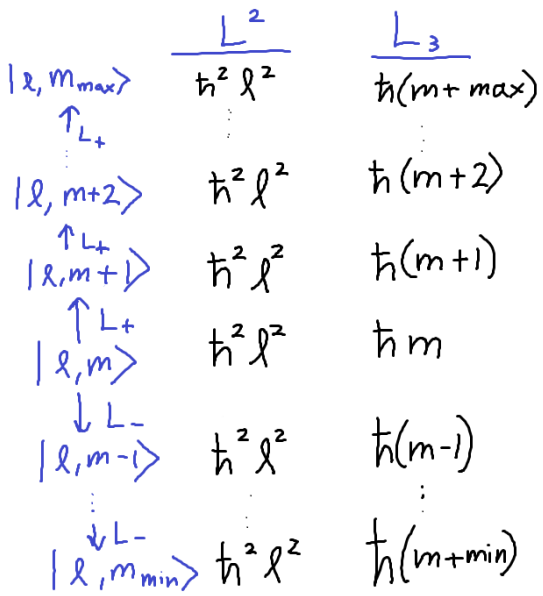
This shows that $L_+ |l, m\rangle$ is also an eigenvector of L_3 with eigenvalue of $\hbar(m+1)$.

If we do these same two operations with L_- we find the following:

$$L^2(L_- |l, m\rangle) = \hbar^2 l^2 (L_- |l, m\rangle) \tag{67}$$

$$L_3 L_- |l, m\rangle = -\hbar L_- |l, m\rangle + \hbar m L_- |l, m\rangle = \hbar(m-1)(L_- |l, m\rangle) \tag{68}$$

We can make a table for these results:



The restriction we found ($m^2 \leq l^2 \implies |m| \leq |l|$) means that at some point this set of eigenvectors produced by L_+ and L_- must be finite, meaning that:

$$L_+ |l, m_{max}\rangle = 0 \tag{69}$$

$$L_- |l, m_{min}\rangle = 0 \tag{70}$$

So, we can write (no one is stopping us):

$$\begin{aligned} L_- L_+ |l, m_{max}\rangle = 0 = (L_1 - iL_2)(L_1 + iL_2) |l, m_{max}\rangle \\ = [L_1^2 + L_2^2 + i(L_1 L_2 - L_2 L_1)] |l, m_{max}\rangle = [L_1^2 + L_2^2 + i(i\hbar L_3)] |l, m_{max}\rangle \\ = [L^2 - L_3^2 - \hbar L_3] |l, m_{max}\rangle \\ = [\hbar^2 l^2 - \hbar^2 m_{max}^2 - \hbar^2 m_{max}] |l, m_{max}\rangle = 0 \end{aligned} \tag{71}$$

$$\implies l^2 = m_{max}^2 + m_{max} \tag{72}$$

We would have guessed that $l^2 = m_{max}^2$ (because at max we say all angular momentum is in one direction and think they behave like typical vectors we are used to in classical mechanics) but this is not the case.

Similarly we can use the lower bound to solve:

$$\begin{aligned} L_+ L_- |l, m_{min}\rangle = 0 = (L_1^2 + L_2^2 + i(L_2 L_1 - L_1 L_2)) |l, m_{min}\rangle \\ = [\hbar^2 l^2 - \hbar^2 m_{min}^2 + \hbar^2 m_{min}] |l, m_{min}\rangle = 0 \end{aligned} \tag{73}$$

$$\implies l^2 = m_{min}^2 - m_{min} \tag{74}$$

Remembering that l is fixed (we are finding the set of solutions for a given total angular momentum):

$$m_{max}^2 + m_{max} = m_{min}^2 - m_{min} \tag{75}$$

Two solutions to this equations are:

$$1)\ \cancel{m_{max} = m_{min} - 1} \tag{76}$$

$$2)\ m_{max} = -m_{min} \tag{77}$$

However, only the second solution is physically valid because $m_{max} \geq m_{min}$.

We now understand that if we have an eigenvector of a certain value of m, L_+, in essence, brings us to a new eigenvector of L^2 and L_3 with $m_{+1} = m + 1$ and L_- brings us to an eigenvector of L^2 and L_3 with $m_{-1} = m - 1$.

This all leads us to conclude:

$$m_{max} - m_{min} = 2m_{max} = \text{some non-negative integer} \tag{78}$$

Let's recall that $L_1 = L_x = -i\hbar[y\frac{\partial}{\partial z} - z\frac{\partial}{\partial z}]$, $L_2 = L_y = -i\hbar[z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}]$, and $L_3 = L_z = -i\hbar[x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}]$, yet we did not solve a differential equation to find this solution set!

From now on, we will denote $m_{max} \equiv j$ and we know that $2j$ must be some integer so:

$$j = 0, \frac{1}{2}, 1, \frac{3}{2}, 2, \frac{5}{2}, ... \tag{79}$$

2 Diving deeper into the physical meaning of these operators

We know now that L^2 operates on wave function with a resulting eigenvalue of l^2 which we can rewrite as the following based on our new definition of j:

$$L^2 |j, m\rangle = \hbar^2 j(j+1) |j, m\rangle \tag{80}$$

This is a hermitian operator, which implies the following based on the proof at the top of page 21 of QN 4:

$$\implies \langle j_1, m_1 | j_2, m_2 \rangle = 0 \text{ if } j_1 \neq j_2 \tag{81}$$

Similarly for L_3:

$$L_3 |j, m\rangle = \hbar m |j, m\rangle \tag{82}$$

$$\implies \langle j_1, m_1 | j_2, m_2 \rangle = 0 \text{ if } m_1 \neq m_2 \tag{83}$$

Combining these two:

$$\langle j_1 m_1 | j_2 m_2 \rangle = 0 \text{ if } j_1 \neq j_2 \text{ or } m_1 \neq m_2 \tag{84}$$

We will also set the normalization such that $\langle jm|jm\rangle = 1$.

2.1 Understanding the difference between classical and quantum angular momentum, the nuance of the operator

Classical Mechanics angular momentum looks like the following:

$$\vec{L} = L_1\hat{i} + L_2\hat{j} + L_3\hat{k} \tag{85}$$

$$\frac{d\vec{L}}{dt} = 0 \text{ so we can pick } \vec{L} = L\hat{k} \tag{86}$$

Given this intuition from classical mechanics, we would expect that in quantum/wave mechanics $\vec{L} \times \vec{L} = 0$ but let's try it:

$$\begin{aligned} \vec{L} \times \vec{L} &= (L_1\hat{i} + L_2\hat{j} + L_3\hat{k}) \times (L_1\hat{i} + L_2\hat{j} + L_3\hat{k}) \\ &= L_1L_2\hat{k} - L_1L_3\hat{j} + L_2L_3\hat{i} - L_2L_1\hat{k} + L_3L_1\hat{j} - L_3L_2\hat{i} \\ &= (L_2L_3 - L_3L_2)\hat{i} + (L_3L_1 - L_1L_3)\hat{j} + (L_1L_2 - L_2L_1)\hat{k} \\ &= i\hbar L_1\hat{i} + i\hbar L_2\hat{j} + i\hbar L_3\hat{k} = i\hbar\vec{L} \end{aligned} \tag{87}$$

Does not match expectations! So let's dive more closely into what this angular momentum "$\vec{L}$" really is, how it compares to l and what that really means for an experimentalist.

2.2 Experimentalist's Perspective

Let's say an experimentalist measures angular momentum of some particle whose wave function we will call s. They would measure $\vec{l}$ as follows:

$$\begin{aligned} \vec{l} &= \text{Measurement of operator} = \langle s|\vec{L}|s\rangle \\ &= (\langle s|L_1|s\rangle)\hat{i} + (\langle s|L_2|s\rangle)\hat{j} + (\langle s|L_3|s\rangle)\hat{k} \end{aligned} \tag{88}$$

Taking this measured value of angular momentum, $\vec{l}$, and crossing it with itself:

$$\vec{l} \times \vec{l} = 0 \tag{89}$$

Therefore, the experimentalist is not confused at all!

Now, let's think about the dot product of the angular momentum measurement($\vec{l}$) with itself (a bit different from in classical mechanics where we would be thinking about $\vec{L} \cdot \vec{L} = L^2$):

$$\vec{l} \cdot \vec{l} = (\langle s|L_1|s\rangle)^2\hat{i} + (\langle s|L_2|s\rangle)^2\hat{j} + (\langle s|L_3|s\rangle)^2\hat{k} \tag{90}$$

Let's try to solve this. First, understanding what the operator L_1^2 is and what it does:

$$\langle s|(L_1(L_1|s\rangle)) = \langle s|L_1^2|s\rangle \tag{91}$$

The question is: Is this equal to $= (\langle s|L_1|s\rangle)^2$? Let's try to find out. First applying the operator one time:

$$\langle jm|L_3|jm\rangle = \langle jm|(\hbar m|jm\rangle) = \hbar m \langle jm|jm\rangle \tag{92}$$

Then, if we apply the operator twice, we simply extract $\hbar m$ from the eigenvector twice, and are left with only $\hbar^2 m^2$. This is the same as having found this expectation value twice and multiplied them together, so it is indeed the same as $(\langle jm|L_3|jm\rangle)^2$:

$$\langle jm|L_3^2|jm\rangle = \hbar^2 m^2 = (\langle jm|L_3|jm\rangle)^2 \tag{93}$$

The expectation value of L^2 is as follows (found previously):

$$\langle jm|L^2|jm\rangle = \hbar^2 j(j+1) \tag{94}$$

Now, we can write the addition of the square of the other two angular momentum projections through these other two known operators:

$$\langle jm|L_1^2 + L_2^2|jm\rangle = \langle jm|L^2 - L_3^2|jm\rangle = \hbar^2[j(j+1) - m^2] \tag{95}$$

To find more eigenvectors that satisfy this system it will help to remember these operators:

$$L_+ = L_1 + iL_2 \tag{96}$$

Where $L_+ |j,m\rangle \propto |j,m+1\rangle$
And:

$$L_- = L_1 - iL_2 \tag{97}$$

Where $L_1 |j,m\rangle \propto |j,m-1\rangle$
We can thus write the angular momentum projection L_1 in terms of these operators:

$$\langle jm|L_1|jm\rangle = \frac{1}{2}(\langle jm|L_+|jm\rangle + \langle jm|L_-|jm\rangle) = \frac{1}{2}(0+0) = 0 \tag{98}$$

Since L_1 and L_2 can be rewritten in terms of L_+ and L_-, there value must be zero:

$$l_1 = 0 \tag{99}$$

$$l_2 = 0 \tag{100}$$

$$l_3 = \hbar m \tag{101}$$

So, What does l^2 (or $\vec{l}\cdot\vec{l}$ equal? Is it $\langle jm|L^2|jm\rangle$ or $\langle jm|L|jm\rangle \cdot \langle jm|L|jm\rangle$? The answer that it is not $\langle s|L^2|s\rangle$ because this is the "measured value of x^2" which is not the same as "(measured value of x)^2"

Going back to what we did before:

$$\text{Measured value of } x = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} x e^{\frac{-x^2}{2}} dx = 0 \tag{102}$$

$$\implies (\text{Measured value of } x)^2 = 0 \tag{103}$$

So, this is why the experimentalist still sees the correct dot product of the angular momentum they measured, where $\vec{l}\cdot\vec{l} = 0$. But, the operator L^2 when applied does not result in 0 but rather in $\hbar^2 j(j+1)$.

We'll now focus on solutions for $j = 1$. It has the vectors/functions $|j,m\rangle = |1,-1\rangle, |1,0\rangle, |1,1\rangle$

$$\begin{aligned} \langle j_2, m_2|L_1 L^2|j_1, m_1\rangle &= \hbar^2 j_1(j_1+1)\langle j_2, m_2|L_1|j_1, m_1\rangle \\ = \langle j_2, m_2|L^2 L_1|j_1, m_1\rangle &= \hbar^2 j_2(j_2+1)\langle j_2, m_2|L_1|j_1, m_1\rangle \end{aligned} \tag{104}$$

Subtracting these two equivalent expressions we find:

$$\langle j_2, m_2|L_1|j_1, m_1\rangle \hbar^2[j_1(j_1+1) - j_2(j_2+1)] = 0 \tag{105}$$

$$\implies \langle j_2, m_2|L_1|j_1, m_1\rangle = 0 \text{ if } j_1 \neq j_2 \tag{106}$$

So we must have the same j value in order to find a value for the angular momentum projection.

The same process can be repeated for L_2 to find:

$$\implies \langle j_2, m_2|L_2|j_1, m_1\rangle = 0 \text{ if } j_1 \neq j_2 \tag{107}$$

Recalling operators (96) and (97), we remember these are proportional to new eigenvectors and we will now define the proportionality constants as follows:

$$L_+ |j, m\rangle = n_{+jm} |j, m+1\rangle \tag{108}$$

$$L_- |j, m\rangle = n_{-jm} |j, m-1\rangle \tag{109}$$

Where $n_{+j,m}$ and $n_{-j,m}$ are some real and positive constants. This is a choice we make. We can also write the conjugate of these:

$$\langle j, m| L_\pm^\dagger = n_{\pm jm} \langle j, m+1| \tag{110}$$

Using this conjugate we find:

$$(\langle j, m| |L_\mp)(L_\pm |j, m\rangle) = n_{\pm jm}^2 \langle j, m \pm 1|j, m \pm 1\rangle \tag{111}$$

$$\implies \langle j, m| (L_1 \mp iL_2)(L_1 \pm iL_2) |j, m\rangle = \langle j, m|L_1^2 + L_2^2 \mp \hbar L_3|j, m\rangle \tag{112}$$

$$\implies \langle j, m| L_1^2 + L_2^2 \pm i(L_1L_2 - L_2L_1) |j, m\rangle = \langle j, m|L^2 - L_3^2 \mp \hbar L_3|j, m\rangle \tag{113}$$

$$\implies \langle j, m|\hbar^2 j(j+1) - \hbar m^2 \mp \hbar^2 m|j, m\rangle = \hbar^2[j(j+1) - m^2 \mp m] \langle j, m|j, m\rangle \tag{114}$$

$$\therefore n_{\pm jm}^2 = \hbar^2[j(j+1) - m(m \pm 1)] \tag{115}$$

So now we have a value for this constant!

Let's check that this constant makes sense for L_+ when m=j:

$$L_+ |j, m\rangle = \hbar\sqrt{j(j+1) - m(m+1)} \, |j, m+1\rangle \tag{116}$$

$$L_+ |j, j\rangle = 0 \tag{117}$$

This 0 is the expected result (because at $j,\vec{j}$ we reach the max value of m allowed for a given j so performing L_+ should result in 0). So we did not make a mistake in the algebra.

Similarly for L_-:

$$L_- |j, m\rangle = \hbar\sqrt{j(j+1) - m(m-1)} \, |j, m-1\rangle \tag{118}$$

$$L_- |j, -j\rangle = 0 \tag{119}$$

We can use L_+ and L_- to rewrite our L_1 and L_2:

$$L_1 = \frac{L_+ + L_-}{2} \tag{120}$$

$$L_2 = \frac{L_+ - L_-}{2i} \tag{121}$$

$$L_1 |j,m\rangle = \frac{1}{2}L_+ |j,m\rangle + \frac{1}{2}L_- |j,m\rangle$$
$$= \frac{\hbar}{2}\sqrt{j(j+1)-m(m+1)}\,|j,m+1\rangle + \frac{\hbar}{2}\sqrt{j(j+1)-m(m-1)}\,|j,m-1\rangle \tag{122}$$

$$L_2 |j,m\rangle = \frac{-i}{2}L_+ |j,m\rangle + \frac{i}{2}L_- |j,m\rangle$$
$$= \frac{-i\hbar}{2}\sqrt{j(j+1)-m(m+1)}\,|j,m+1\rangle + \frac{i\hbar}{2}\sqrt{j(j+1)-m(m-1)}\,|j,m-1\rangle \tag{123}$$

Note: Unitary Operators
Let's imagine an operator O acting on a vector u:

$$O |u\rangle = |v\rangle \tag{124}$$

Where:

$$|u\rangle = u_i |i\rangle \tag{125}$$
$$|v\rangle = v_i |i\rangle \tag{126}$$

We know that in this basis:

$$\langle j|i\rangle = \delta_{ij} \tag{127}$$

$$O |u\rangle = \sum_i u_i O |i\rangle = \sum_j v_j |j\rangle \tag{128}$$

$$\langle k|O|u\rangle = \sum_i u_i \langle k|O|i\rangle = \sum_j v_j \langle k|j\rangle = \sum_j v_j \delta_{kj} = v_k \tag{129}$$

In conclusion:

$$\sum_i (\langle k|O|i\rangle) u_i = v_k \tag{130}$$

$\langle k|O|i\rangle$ looks like a matrix that's multiplying u_i, so we'll call it O_{ki}.

Applying what we learned above to the L_3 operator:

$$\begin{aligned}\langle j_1 m_1|L_3|j_2 m_2\rangle &= \hbar m \langle j_1 m_1|j_2 m_2\rangle \\ &= \hbar m_2 \delta_{j_1 j_2}\delta_{m_1 m_2} = (L_3)_{j_1 m_1, j_2 m_2}\end{aligned} \tag{131}$$

So we're left with a matrix $(L_3)_{j_1 m_1, j_2 m_2}$ (diagonal matrix in this case) with which we can represent what this operator does.

Similarly for L_1:

$$\begin{aligned}&\langle j_1, m_1|L_1|j_2, m_2\rangle \\ &= \frac{\hbar}{2}\sqrt{j_2(j_2+1)-m_2(m_2+1)}\,\langle j_1, m_1|j_2, m_2+1\rangle + \frac{\hbar}{2}\sqrt{j_2(j_2+1)-m_2(m_2-1)}\,\langle j_1, m_1|j_2, m_2-1\rangle \\ &= \frac{\hbar}{2}\sqrt{j_2(j_2+1)-m_2(m_2+1)}\delta_{j_1,j_2}\delta_{m_1,m_2+1} + \frac{\hbar}{2}\sqrt{j_2(j_2+1)-m_2(m_2-1)}\delta_{j_1,j_2}\delta_{m_1,m_2-1}\end{aligned} \tag{132}$$

And finally for L_2:

$$\langle j_1, m_1|L_2|j_2, m_2\rangle = \frac{-i\hbar}{2}\sqrt{j_2(j_2+1)-m_2(m_2+1)}\delta_{j_1,j_2}\delta_{m_1,m_2+1} + \frac{i\hbar}{2}\sqrt{j_2(j_2+1)-m_2(m_2-1)}\delta_{j_1,j_2}\delta_{m_1,m_2-1} \tag{133}$$

In summary:

$$(L_1)_{j_1 m_1, j_2 m_2} = \frac{\hbar}{2}\sqrt{j_2(j_2+1)-m_2(m_2+1)}\delta_{j_1,j_2}\delta_{m_1,m_2+1} + \frac{\hbar}{2}\sqrt{j_2(j_2+1)-m_2(m_2-1)}\delta_{j_1,j_2}\delta_{m_1,m_2-1} \tag{134}$$

$$(L_2)_{j_1 m_1, j_2 m_2} = \frac{-i\hbar}{2}\sqrt{j_2(j_2+1)-m_2(m_2+1)}\delta_{j_1,j_2}\delta_{m_1,m_2+1} + \frac{i\hbar}{2}\sqrt{j_2(j_2+1)-m_2(m_2-1)}\delta_{j_1,j_2}\delta_{m_1,m_2-1} \tag{135}$$

$$(L_3)_{j_1 m_1, j_2 m_2} = \hbar m_2 \delta_{j_1 j_2}\delta_{m_1 m_2} \tag{136}$$

3 Matrix Solutions

3.1 j=1 and m=-1,0,1

If j=1, our solutions above simplify to:

$$(L_1)_{m_1,m_2} = \frac{\hbar}{2}\sqrt{2-m_2(m_2+1)}\delta_{m_1,m_2+1} + \frac{\hbar}{2}\sqrt{2-m_2(m_2-1)}\delta_{m_1,m_2-1} \tag{137}$$

$$(L_2)_{m_1,m_2} = \frac{-i\hbar}{2}\sqrt{2-m_2(m_2+1)}\delta_{m_1,m_2+1} + \frac{i\hbar}{2}\sqrt{2-m_2(m_2-1)}\delta_{m_1,m_2-1} \tag{138}$$

$$(L_3)_{m_1,m_2} = \hbar m_2 \delta_{m_1 m_2} \tag{139}$$

Plugging in various values for m_1 and m_2 (j_1 and j_2 must be the same for all of these operators) into the expressions of each and making that into a matrix:

$$(L_1)_{m_1m_2} = \begin{pmatrix} 0 & \frac{\hbar}{\sqrt{2}} & 0 \\ \frac{\hbar}{\sqrt{2}} & 0 & \frac{\hbar}{\sqrt{2}} \\ 0 & \frac{\hbar}{\sqrt{2}} & 0 \end{pmatrix} \tag{140}$$

$$(L_2)_{m_1m_2} = \begin{pmatrix} 0 & \frac{i\hbar}{\sqrt{2}} & 0 \\ \frac{-i\hbar}{\sqrt{2}} & 0 & \frac{i\hbar}{\sqrt{2}} \\ 0 & \frac{-i\hbar}{\sqrt{2}} & 0 \end{pmatrix} \tag{141}$$

$$(L_3)_{m_1m_2} = \begin{pmatrix} -\hbar & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & \hbar \end{pmatrix} \tag{142}$$

$$(L_1)^2_{m_1m_2} = \begin{pmatrix} \frac{\hbar^2}{2} & 0 & \frac{\hbar^2}{2} \\ 0 & \hbar^2 & 0 \\ \frac{\hbar^2}{2} & 0 & \frac{\hbar^2}{2} \end{pmatrix} \tag{143}$$

$$(L_2)^2_{m_1m_2} = \begin{pmatrix} \frac{\hbar^2}{2} & 0 & \frac{-\hbar^2}{2} \\ 0 & \hbar^2 & 0 \\ \frac{-\hbar^2}{2} & 0 & \frac{-\hbar^2}{2} \end{pmatrix} \tag{144}$$

$$(L_3)^2_{m_1m_2} = \begin{pmatrix} \hbar^2 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & \hbar^2 \end{pmatrix} \tag{145}$$

$$(L)^2_{m_1m_2} = \begin{pmatrix} 2\hbar^2 & 0 & 0 \\ 0 & 2\hbar^2 & 0 \\ 0 & 0 & 2\hbar^2 \end{pmatrix} = 2\hbar^2\mathbb{1} \tag{146}$$

From this last matrix we can see that $j(j+1)\hbar^2 = 2\hbar^2$ when $j = 1$, as we expected so it seems this matrix is correct.

So, why are L_1^2 and L_2^2 not diagonal?

$$[L^2, L_1] = 0 \tag{147}$$

$$[L^2, L_1^2] = 0 \tag{148}$$

$$[L_1^2, L_3] \neq 0 \tag{149}$$

$$[L_2^2, L_3] \neq 0 \tag{150}$$

Now, another thing we can do with these matrices to see if they are consistent is check commutators. Checking that $[L_1, L_2] = i\hbar L_3$:

$$L_1L_2 = \hbar^2 \begin{pmatrix} \frac{-i}{2} & 0 & \frac{i}{2} \\ 0 & 0 & 0 \\ \frac{-i}{2} & 0 & \frac{-i}{2} \end{pmatrix} \tag{151}$$

$$L_2L_1 = \hbar^2 \begin{pmatrix} \frac{i}{2} & 0 & \frac{i}{2} \\ 0 & 0 & 0 \\ \frac{-i}{2} & 0 & \frac{-i}{2} \end{pmatrix} \tag{152}$$

$$[L_1, L_2] = L_1L_2 - L_2L_1 = \hbar^2 \begin{pmatrix} -i & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & i \end{pmatrix} = i\hbar \begin{pmatrix} -1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix} = i\hbar L_3 \tag{153}$$

Indeed, $[L_1, L_2] = i\hbar L_3$!

3.2 j=1/2 and m=-1/2,1/2

If $j = 1/2$, our solutions above simplify to:

$$(L_1)_{m_1,m_2} = \frac{\hbar}{2}\sqrt{\frac{3}{4} - m_2(m_2+1)}\delta_{m_1,m_2+1} + \frac{\hbar}{2}\sqrt{\frac{3}{4} - m_2(m_2-1)}\delta_{m_1,m_2-1} \tag{154}$$

$$(L_2)_{j_1m_1,j_2m_2} = \frac{-i\hbar}{2}\sqrt{\frac{3}{4} - m_2(m_2+1)}\delta_{m_1,m_2+1} + \frac{i\hbar}{2}\sqrt{\frac{3}{4} - m_2(m_2-1)}\delta_{m_1,m_2-1} \tag{155}$$

$$(L_3)_{m_1,m_2} = \hbar m_2 \delta_{m_1m_2} \tag{156}$$

So, our matrices are:

$$(L_1)_{m_1m_2} = \begin{pmatrix} 0 & \frac{\hbar}{2} \\ \frac{\hbar}{2} & 0 \end{pmatrix} \tag{157}$$

$$(L_2)_{m_1m_2} = \begin{pmatrix} 0 & \frac{i\hbar}{2} \\ \frac{-i\hbar}{2} & 0 \end{pmatrix} \tag{158}$$

$$(L_3)_{m_1m_2} = \begin{pmatrix} -\frac{\hbar}{2} & 0 \\ 0 & \frac{\hbar}{2} \end{pmatrix} \tag{159}$$

$$(L_1)^2_{m_1m_2} = \begin{pmatrix} 0 & \frac{\hbar}{2} \\ \frac{\hbar}{2} & 0 \end{pmatrix} \begin{pmatrix} 0 & \frac{\hbar}{2} \\ \frac{\hbar}{2} & 0 \end{pmatrix} = \begin{pmatrix} \frac{\hbar^2}{4} & 0 \\ 0 & \frac{\hbar^2}{4} \end{pmatrix} \tag{160}$$

$$(L_2)^2_{m_1m_2} = \begin{pmatrix} 0 & \frac{i\hbar}{2} \\ \frac{-i\hbar}{2} & 0 \end{pmatrix} \begin{pmatrix} 0 & \frac{i\hbar}{2} \\ \frac{-i\hbar}{2} & 0 \end{pmatrix} = \begin{pmatrix} \frac{\hbar^2}{4} & 0 \\ 0 & \frac{\hbar^2}{4} \end{pmatrix} \tag{161}$$

$$(L_3)^2_{m_1m_2} = \begin{pmatrix} -\frac{\hbar}{2} & 0 \\ 0 & \frac{\hbar}{2} \end{pmatrix} \begin{pmatrix} -\frac{\hbar}{2} & 0 \\ 0 & \frac{\hbar}{2} \end{pmatrix} = \begin{pmatrix} \frac{\hbar^2}{4} & 0 \\ 0 & \frac{\hbar^2}{4} \end{pmatrix} \tag{162}$$

$$L^2 = L_x^2 + L_y^2 + L_z^2 = \frac{3}{4}\hbar^2 \mathbb{1} \tag{163}$$

3.3 j=3/2 and m=-3/2,-1/2,1/2,3/2

If $j = 3/2$, our solutions above simplify to:

$$(L_1)_{m_1,m_2} = \frac{\hbar}{2}\sqrt{\frac{15}{4} - m_2(m_2+1)}\delta_{m_1,m_2+1} + \frac{\hbar}{2}\sqrt{\frac{15}{4} - m_2(m_2-1)}\delta_{m_1,m_2-1} \tag{164}$$

$$(L_2)_{j_1m_1,j_2m_2} = \frac{-i\hbar}{2}\sqrt{\frac{15}{4} - m_2(m_2+1)}\delta_{m_1,m_2+1} + \frac{i\hbar}{2}\sqrt{\frac{15}{4} - m_2(m_2-1)}\delta_{m_1,m_2-1} \tag{165}$$

$$(L_3)_{m_1,m_2} = \hbar m_2 \delta_{m_1 m_2} \tag{166}$$

$$(L_1)_{m_1m_2} = \begin{pmatrix} 0 & \frac{\sqrt{3}\hbar}{2} & 0 & 0 \\ \frac{\sqrt{3}\hbar}{2} & 0 & \frac{2\hbar}{2} & 0 \\ 0 & \frac{2\hbar}{2} & 0 & \frac{\sqrt{3}\hbar}{2} \\ 0 & 0 & \frac{\sqrt{3}\hbar}{2} & 0 \end{pmatrix} \tag{167}$$

$$(L_2)_{m_1m_2} = \begin{pmatrix} 0 & \frac{i\sqrt{3}\hbar}{2} & 0 & 0 \\ \frac{-i\sqrt{3}\hbar}{2} & 0 & \frac{i2\hbar}{2} & 0 \\ 0 & \frac{-i2\hbar}{2} & 0 & \frac{i\sqrt{3}\hbar}{2} \\ 0 & 0 & \frac{-i\sqrt{3}\hbar}{2} & 0 \end{pmatrix} \tag{168}$$

$$(L_3)_{m_1m_2} = \begin{pmatrix} \frac{-3\hbar}{2} & 0 & 0 & 0 \\ 0 & \frac{-\hbar}{2} & 0 & 0 \\ 0 & 0 & \frac{\hbar}{2} & \hbar \\ 0 & 0 & 0 & \frac{3\hbar}{2} \end{pmatrix} \tag{169}$$

$$(L_1)^2_{m_1m_2} = \begin{pmatrix} 0 & \frac{\sqrt{3}\hbar}{2} & 0 & 0 \\ \frac{\sqrt{3}\hbar}{2} & 0 & \frac{2\hbar}{2} & 0 \\ 0 & \frac{2\hbar}{2} & 0 & \frac{\sqrt{3}\hbar}{2} \\ 0 & 0 & \frac{\sqrt{3}\hbar}{2} & 0 \end{pmatrix}^2 = \begin{pmatrix} \frac{3\hbar^2}{4} & 0 & \frac{\sqrt{3}\hbar^2}{2} & 0 \\ 0 & \frac{7\hbar^2}{4} & 0 & \frac{\sqrt{3}\hbar^2}{2} \\ \frac{\sqrt{3}\hbar^2}{2} & 0 & \frac{7\hbar^2}{4} & 0 \\ 0 & \frac{\sqrt{3}\hbar^2}{2} & 0 & \frac{3\hbar^2}{4} \end{pmatrix} \tag{170}$$

$$(L_2)^2_{m_1m_2} = \begin{pmatrix} 0 & \frac{i\sqrt{3}\hbar}{2} & 0 & 0 \\ \frac{-i\sqrt{3}\hbar}{2} & 0 & \frac{i2\hbar}{2} & 0 \\ 0 & \frac{-i2\hbar}{2} & 0 & \frac{i\sqrt{3}\hbar}{2} \\ 0 & 0 & \frac{-i\sqrt{3}\hbar}{2} & 0 \end{pmatrix}^2 = \begin{pmatrix} \frac{3\hbar^2}{4} & 0 & \frac{-\sqrt{3}\hbar^2}{2} & 0 \\ 0 & \frac{7\hbar^2}{4} & 0 & \frac{-\sqrt{3}\hbar^2}{2} \\ \frac{-\sqrt{3}\hbar^2}{2} & 0 & \frac{7\hbar^2}{4} & 0 \\ 0 & \frac{-\sqrt{3}\hbar^2}{2} & 0 & \frac{3\hbar^2}{4} \end{pmatrix} \tag{171}$$

$$(L_3)_{m_1m_2} = \begin{pmatrix} \frac{-3\hbar}{2} & 0 & 0 & 0 \\ 0 & \frac{-\hbar}{2} & 0 & 0 \\ 0 & 0 & \frac{\hbar}{2} & \hbar \\ 0 & 0 & 0 & \frac{3\hbar}{2} \end{pmatrix}^2 = \begin{pmatrix} \frac{9\hbar^2}{4} & 0 & 0 & 0 \\ 0 & \frac{\hbar^2}{4} & 0 & 0 \\ 0 & 0 & \frac{\hbar^2}{4} & \hbar \\ 0 & 0 & 0 & \frac{9\hbar^2}{4} \end{pmatrix} \tag{172}$$

$$L^2 = L_x^2 + L_y^2 + L_z^2 = \frac{15}{4}\hbar^2 \mathbb{1} \tag{173}$$

3.4 j=2 and m=-2,-1,0,1,2

$$(L_1)_{m_1,m_2} = \frac{\hbar}{2}\sqrt{6 - m_2(m_2+1)}\delta_{m_1,m_2+1} + \frac{\hbar}{2}\sqrt{6 - m_2(m_2-1)}\delta_{m_1,m_2-1} \tag{174}$$

$$(L_2)_{j_1 m_1, j_2 m_2} = \frac{-i\hbar}{2}\sqrt{6 - m_2(m_2+1)}\delta_{m_1,m_2+1} + \frac{i\hbar}{2}\sqrt{6 - m_2(m_2-1)}\delta_{m_1,m_2-1} \tag{175}$$

$$(L_3)_{m_1,m_2} = \hbar m_2 \delta_{m_1 m_2} \tag{176}$$

$$(L_1)_{m_1 m_2} = \begin{pmatrix} 0 & \hbar & 0 & 0 & 0 \\ \hbar & 0 & \frac{\sqrt{6}}{2}\hbar & 0 & 0 \\ 0 & \frac{\sqrt{6}}{2}\hbar & 0 & \frac{\sqrt{6}}{2}\hbar & 0 \\ 0 & 0 & \frac{\sqrt{6}}{2}\hbar & 0 & \hbar \\ 0 & 0 & 0 & \hbar & 0 \end{pmatrix} \tag{177}$$

$$(L_2)_{m_1 m_2} = \begin{pmatrix} 0 & i\hbar & 0 & 0 & 0 \\ -i\hbar & 0 & \frac{i\sqrt{6}}{2}\hbar & 0 & 0 \\ 0 & \frac{-i\sqrt{6}}{2}\hbar & 0 & \frac{i\sqrt{6}}{2}\hbar & 0 \\ 0 & 0 & \frac{-i\sqrt{6}}{2}\hbar & 0 & i\hbar \\ 0 & 0 & 0 & -i\hbar & 0 \end{pmatrix} \tag{178}$$

$$(L_3)_{m_1 m_2} = \begin{pmatrix} -2\hbar & 0 & 0 & 0 & 0 \\ 0 & -\hbar & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & \hbar & 0 \\ 0 & 0 & 0 & 0 & 2\hbar \end{pmatrix} \tag{179}$$

$$(L_1)^2_{m_1 m_2} = \begin{pmatrix} 0 & \hbar & 0 & 0 & 0 \\ \hbar & 0 & \frac{\sqrt{6}}{2}\hbar & 0 & 0 \\ 0 & \frac{\sqrt{6}}{2}\hbar & 0 & \frac{\sqrt{6}}{2}\hbar & 0 \\ 0 & 0 & \frac{\sqrt{6}}{2}\hbar & 0 & \hbar \\ 0 & 0 & 0 & \hbar & 0 \end{pmatrix}^2 = \begin{pmatrix} \hbar^2 & 0 & \frac{\sqrt{6}}{2}\hbar^2 & 0 & 0 \\ 0 & \frac{5}{2}\hbar^2 & 0 & \frac{3}{2}\hbar^2 & 0 \\ \frac{\sqrt{6}}{2}\hbar^2 & 0 & 3\hbar^2 & 0 & \frac{\sqrt{6}}{2}\hbar^2 \\ 0 & \frac{3}{2}\hbar^2 & 0 & \frac{5}{2}\hbar^2 & 0 \\ 0 & 0 & \frac{\sqrt{6}}{2}\hbar^2 & 0 & \hbar^2 \end{pmatrix} \tag{180}$$

$$(L_2)^2_{m_1 m_2} = \begin{pmatrix} 0 & i\hbar & 0 & 0 & 0 \\ -i\hbar & 0 & i\sqrt{6}\hbar & 0 & 0 \\ 0 & -i\sqrt{6}\hbar & 0 & i\sqrt{6}\hbar & 0 \\ 0 & 0 & -i\sqrt{6}\hbar & 0 & i\hbar \\ 0 & 0 & 0 & -i\hbar & 0 \end{pmatrix}^2 = \begin{pmatrix} \hbar^2 & 0 & \frac{-\sqrt{6}}{2}\hbar^2 & 0 & 0 \\ 0 & \frac{5}{2}\hbar^2 & 0 & \frac{-3}{2}\hbar^2 & 0 \\ \frac{-\sqrt{6}}{2}\hbar^2 & 0 & 3\hbar^2 & 0 & \frac{-\sqrt{6}}{2}\hbar^2 \\ 0 & \frac{-3}{2}\hbar^2 & 0 & \frac{5}{2}\hbar^2 & 0 \\ 0 & 0 & \frac{-\sqrt{6}}{2}\hbar^2 & 0 & \hbar^2 \end{pmatrix} \tag{181}$$

$$(L_3)^2_{m_1 m_2} = \begin{pmatrix} -2\hbar & 0 & 0 & 0 & 0 \\ 0 & -\hbar & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & \hbar & 0 \\ 0 & 0 & 0 & 0 & 2\hbar \end{pmatrix}^2 = \begin{pmatrix} 4\hbar^2 & 0 & 0 & 0 & 0 \\ 0 & \hbar & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & \hbar & 0 \\ 0 & 0 & 0 & 0 & 4\hbar^2 \end{pmatrix} \tag{182}$$

$$L^2 = L_x^2 + L_y^2 + L_z^2 = 6\hbar^2 \mathbb{1} \tag{183}$$

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Let's say our experiments can measure j but not m, a "Rotor Model."

Remember eigenvectors depend on time like $e^{\frac{-iE}{\hbar}t}$

At time $t = 0$:

$$c_1 |E_1\rangle + c_2 |E_2\rangle \tag{184}$$

$$c_1 |j_1, m_1\rangle + c_2 |j_2, m_2\rangle \tag{185}$$

Over time this will become:

$$c_1 e^{\frac{-iE(j_1)}{\hbar}t} |E_1\rangle + c_2 e^{\frac{-iE(j_2)}{\hbar}t} |E_2\rangle \tag{186}$$

$$c_1 e^{\frac{-iE(j_1)}{\hbar}t} |j_1, m_1\rangle + c_2 e^{\frac{-iE(j_2)}{\hbar}t} |j_2, m_2\rangle \tag{187}$$

This new state is not proportional to the state at time $t = 0$ <u>if</u> $j_1 \neq j_2$.

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3.5 Changing basis of our Matrix Solutions

Now, for our solution set where $j = 1$, let's switch to finding eigenvalues of $(L_1)_{m_1 m_2}$ in order to find a new basis for this solution set. Taking the determinant and setting to 0:

$$\begin{vmatrix} \lambda & \frac{-\hbar}{\sqrt{2}} & 0 \\ \frac{-\hbar}{\sqrt{2}} & \lambda & \frac{-\hbar}{\sqrt{2}} \\ 0 & \frac{-\hbar}{\sqrt{2}} & \lambda \end{vmatrix} = 0 \tag{188}$$

$$\implies \lambda \left[\lambda^2 - \frac{\hbar^2}{2}\right] + \frac{\hbar}{\sqrt{2}} \left(\frac{-\hbar}{\sqrt{2}}\lambda\right) = 0 \tag{189}$$

$$\implies \lambda \left[\lambda^2 - \frac{\hbar^2}{2} - \frac{\hbar^2}{2}\right] = 0 \tag{190}$$

$$\implies \lambda[\lambda^2 - \hbar^2] = 0 \tag{191}$$

$$\implies \lambda = 0,\ \lambda = \pm\hbar \tag{192}$$

We want to find new transformation matrices and show that the ones we had are arbitrary based on the basis. Our previous basis was:

$$[L_a, L_b] = L_a L_b - L_b L_a = i\hbar \mathcal{E}_{abc} L_c \tag{193}$$

We want to find a change of basis matrix based on the eigenvectors of $(L_1)_{m_1 m_2}$ that we just found. This matrix u will be unitary, meaning it satisfies $u^\dagger u = 1$ because that will allow us to find the new transformation matrix $L_a^{'}$:

$$L_a^{'} = u L_a u^\dagger \tag{194}$$

This new set of transformation matrices will operate just like the previous set did:

$$\begin{gathered} L_a^{'} L_b^{'} - L_b^{'} L_a^{'} = u L_a u^\dagger u L_b u^\dagger - u L_b u^\dagger u L_a u^\dagger \\ = u(L_a L_b - L_b L_a) u^\dagger = u i\hbar \mathcal{E}_{abc} L_c u^\dagger = i\hbar \mathcal{E}_{abc} u L_c u^\dagger \end{gathered} \tag{195}$$

$$\therefore [L_a^{'}, L_b^{'}] = i\hbar \mathcal{E}_{abc} L_c \tag{196}$$

So, let's try to diagonalize L_1. Currently we have:

$$L_1 = \frac{\hbar}{\sqrt{2}} \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix} \tag{197}$$

$$L_2 = \frac{\hbar}{\sqrt{2}} \begin{pmatrix} 0 & i & 0 \\ -i & 0 & i \\ 0 & -i & 0 \end{pmatrix} \tag{198}$$

$$L_3 = \frac{\hbar}{\sqrt{2}} \begin{pmatrix} -1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix} \tag{199}$$

From the matrix $(L_1)_{m_1, m_1}$ for $j = 1$ we get the following eigenvector equation (ignoring the $\frac{\hbar}{\sqrt{2}}$):

$$\begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix} \begin{pmatrix} a \\ b \\ c \end{pmatrix} = \begin{pmatrix} a \\ b \\ c \end{pmatrix} \lambda \tag{200}$$

From this we find that:

$$b = a\lambda \tag{201}$$

$$a + c = b\lambda \tag{202}$$

$$b = c\lambda \tag{203}$$

$$\implies a\lambda + c\lambda = b\lambda^2 \tag{204}$$

$$\implies b + b = b\lambda^2 \implies \lambda^2 = 2 \tag{205}$$

$$\implies \lambda = \pm\sqrt{2} \tag{206}$$

From looking at these equation, $\lambda = 0$ is also a solution.
If $\lambda = 0$, then $b = 0$ and $a + c = 0$:

$$\begin{pmatrix} a \\ b \\ c \end{pmatrix} = \begin{pmatrix} \frac{1}{\sqrt{2}} \\ 0 \\ \frac{-1}{\sqrt{2}} \end{pmatrix} \tag{207}$$

If $\lambda = \sqrt{2}$, then $a + c = \sqrt{2}b$ and $c = \frac{b}{\sqrt{2}}$:

$$\begin{pmatrix} a \\ b \\ c \end{pmatrix} = \begin{pmatrix} \frac{1}{2} \\ \frac{1}{\sqrt{2}} \\ \frac{1}{2} \end{pmatrix} \tag{208}$$

If $\lambda = -\sqrt{2}$, then $a = \frac{-b}{\sqrt{2}}$ and $a + c = -\sqrt{2}b$:

$$\begin{pmatrix} a \\ b \\ c \end{pmatrix} = \begin{pmatrix} \frac{-1}{2} \\ \frac{1}{\sqrt{2}} \\ \frac{-1}{2} \end{pmatrix} \tag{209}$$

Now let's check that these eigenvectors are correct. If we are adding back the $\frac{\hbar}{\sqrt{2}}$ that we have so far been ignoring, the eigenvalues become 0, $\hbar$, and $-\hbar$:

$$\begin{pmatrix} 0 & \frac{\hbar}{\sqrt{2}} & 0 \\ \frac{\hbar}{\sqrt{2}} & 0 & \frac{\hbar}{\sqrt{2}} \\ 0 & \frac{\hbar}{\sqrt{2}} & 0 \end{pmatrix} \begin{pmatrix} \frac{-1}{2} & \frac{1}{\sqrt{2}} & \frac{1}{2} \\ \frac{1}{\sqrt{2}} & 0 & \frac{1}{\sqrt{2}} \\ \frac{-1}{2} & \frac{-1}{\sqrt{2}} & \frac{1}{2} \end{pmatrix} = \begin{pmatrix} \frac{-1}{2} & \frac{1}{\sqrt{2}} & \frac{1}{2} \\ \frac{1}{\sqrt{2}} & 0 & \frac{1}{\sqrt{2}} \\ \frac{-1}{2} & \frac{-1}{\sqrt{2}} & \frac{1}{2} \end{pmatrix} \begin{pmatrix} -\hbar & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & \hbar \end{pmatrix} \tag{210}$$

Therefore our diagonalized L_1 is:

$$\begin{pmatrix} -\hbar & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & \hbar \end{pmatrix} \tag{211}$$

We will denote this matrix of the eigenvectors of this diagonalized L_1 as u and see that $u^\dagger u = I$:

$$\begin{pmatrix} \frac{-1}{2} & \frac{1}{\sqrt{2}} & \frac{-1}{2} \\ \frac{1}{\sqrt{2}} & 0 & \frac{-1}{\sqrt{2}} \\ \frac{1}{2} & \frac{1}{\sqrt{2}} & \frac{1}{2} \end{pmatrix} \begin{pmatrix} \frac{-1}{2} & \frac{1}{\sqrt{2}} & \frac{1}{2} \\ \frac{1}{\sqrt{2}} & 0 & \frac{1}{\sqrt{2}} \\ \frac{-1}{2} & \frac{-1}{\sqrt{2}} & \frac{1}{2} \end{pmatrix} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \tag{212}$$

$$L_1 u = u \begin{pmatrix} -\hbar & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & \hbar \end{pmatrix} \implies u^\dagger L_1 u = \begin{pmatrix} -\hbar & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & \hbar \end{pmatrix} = L_1' \tag{213}$$

What about $u^\dagger L_2 u$?

$$u^\dagger L_2 u = \frac{\hbar}{\sqrt{2}} \begin{pmatrix} \frac{-1}{2} & \frac{1}{\sqrt{2}} & \frac{-1}{2} \\ \frac{1}{\sqrt{2}} & 0 & \frac{-1}{\sqrt{2}} \\ \frac{1}{2} & \frac{1}{\sqrt{2}} & \frac{1}{2} \end{pmatrix} \begin{pmatrix} 0 & i & 0 \\ -i & 0 & i \\ 0 & -i & 0 \end{pmatrix} \begin{pmatrix} \frac{-1}{2} & \frac{1}{\sqrt{2}} & \frac{-1}{2} \\ \frac{1}{\sqrt{2}} & 0 & \frac{-1}{\sqrt{2}} \\ \frac{1}{2} & \frac{1}{\sqrt{2}} & \frac{1}{2} \end{pmatrix} \begin{pmatrix} \frac{-1}{2} & \frac{1}{\sqrt{2}} & \frac{1}{2} \\ \frac{1}{\sqrt{2}} & 0 & \frac{1}{\sqrt{2}} \\ \frac{-1}{2} & \frac{-1}{\sqrt{2}} & \frac{1}{2} \end{pmatrix} \tag{214}$$

$$= \frac{\hbar}{\sqrt{2}} \begin{pmatrix} \frac{-1}{2} & \frac{1}{\sqrt{2}} & \frac{-1}{2} \\ \frac{1}{\sqrt{2}} & 0 & \frac{-1}{\sqrt{2}} \\ \frac{1}{2} & \frac{1}{\sqrt{2}} & \frac{1}{2} \end{pmatrix} \begin{pmatrix} \frac{i}{\sqrt{2}} & 0 & \frac{i}{\sqrt{2}} \\ 0 & -i\sqrt{2} & 0 \\ \frac{-i}{\sqrt{2}} & 0 & \frac{-i}{\sqrt{2}} \end{pmatrix} = \begin{pmatrix} 0 & -i & 0 \\ i & 0 & i \\ 0 & -i & 0 \end{pmatrix} \frac{\hbar}{\sqrt{2}} = L_2' \tag{215}$$

What about $u^\dagger L_3 u$?

$$u^\dagger L_3 u = \hbar \begin{pmatrix} \frac{-1}{2} & \frac{1}{\sqrt{2}} & \frac{-1}{2} \\ \frac{1}{\sqrt{2}} & 0 & \frac{-1}{\sqrt{2}} \\ \frac{1}{2} & \frac{1}{\sqrt{2}} & \frac{1}{2} \end{pmatrix} \begin{pmatrix} -1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} \frac{-1}{2} & \frac{1}{\sqrt{2}} & \frac{1}{2} \\ \frac{1}{\sqrt{2}} & 0 & \frac{1}{\sqrt{2}} \\ \frac{-1}{2} & \frac{-1}{\sqrt{2}} & \frac{1}{2} \end{pmatrix} \tag{216}$$

$$= \hbar \begin{pmatrix} \frac{-1}{2} & \frac{1}{\sqrt{2}} & \frac{-1}{2} \\ \frac{1}{\sqrt{2}} & 0 & \frac{-1}{\sqrt{2}} \\ \frac{1}{2} & \frac{1}{\sqrt{2}} & \frac{1}{2} \end{pmatrix} \begin{pmatrix} \frac{1}{2} & \frac{-1}{\sqrt{2}} & \frac{-1}{2} \\ 0 & 0 & 0 \\ \frac{-1}{2} & \frac{-1}{\sqrt{2}} & \frac{1}{2} \end{pmatrix} = \hbar \begin{pmatrix} 0 & \frac{1}{\sqrt{2}} & 0 \\ \frac{1}{\sqrt{2}} & 0 & \frac{-1}{\sqrt{2}} \\ 0 & \frac{-2}{\sqrt{2}} & 0 \end{pmatrix} = L_3' \tag{217}$$

These three (L_1',L_2', and L_3') must be related through:

$$[L_a', L_b'] = i\hbar \mathcal{E}_{abc} L_c' \tag{218}$$

We can perform these three operators to prove this is indeed true:

$$[L_1', L_2'] = \begin{pmatrix} -\hbar & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & \hbar \end{pmatrix} \begin{pmatrix} 0 & -\frac{i\hbar}{\sqrt{2}} & 0 \\ \frac{i\hbar}{\sqrt{2}} & 0 & \frac{i\hbar}{\sqrt{2}} \\ 0 & -\frac{i\hbar}{\sqrt{2}} & 0 \end{pmatrix} - \begin{pmatrix} 0 & -\frac{i\hbar}{\sqrt{2}} & 0 \\ \frac{i\hbar}{\sqrt{2}} & 0 & \frac{i\hbar}{\sqrt{2}} \\ 0 & -\frac{i\hbar}{\sqrt{2}} & 0 \end{pmatrix} \begin{pmatrix} -\hbar & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & \hbar \end{pmatrix} \tag{219}$$

$$= \begin{pmatrix} 0 & \frac{i\hbar^2}{\sqrt{2}} & 0 \\ 0 & 0 & 0 \\ 0 & -\frac{i\hbar^2}{\sqrt{2}} & 0 \end{pmatrix} - \begin{pmatrix} 0 & 0 & 0 \\ -\frac{i\hbar^2}{\sqrt{2}} & 0 & \frac{i\hbar^2}{\sqrt{2}} \\ 0 & 0 & 0 \end{pmatrix} \tag{220}$$

$$= i\hbar \begin{pmatrix} 0 & \frac{\hbar}{\sqrt{2}} & 0 \\ \frac{\hbar}{\sqrt{2}} & 0 & -\frac{\hbar}{\sqrt{2}} \\ 0 & -\frac{\hbar}{\sqrt{2}} & 0 \end{pmatrix} = i\hbar L_3' \tag{221}$$

The same can be done for L_2' and L_3'

$$[L_2', L_3'] = \begin{pmatrix} 0 & -\frac{i\hbar}{\sqrt{2}} & 0 \\ \frac{i\hbar}{\sqrt{2}} & 0 & \frac{i\hbar}{\sqrt{2}} \\ 0 & -\frac{i\hbar}{\sqrt{2}} & 0 \end{pmatrix} \begin{pmatrix} 0 & \frac{\hbar}{\sqrt{2}} & 0 \\ \frac{\hbar}{\sqrt{2}} & 0 & -\frac{\hbar}{\sqrt{2}} \\ 0 & -\frac{\hbar}{\sqrt{2}} & 0 \end{pmatrix} - \begin{pmatrix} 0 & \frac{\hbar}{\sqrt{2}} & 0 \\ \frac{\hbar}{\sqrt{2}} & 0 & -\frac{\hbar}{\sqrt{2}} \\ 0 & -\frac{\hbar}{\sqrt{2}} & 0 \end{pmatrix} \begin{pmatrix} 0 & -\frac{i\hbar}{\sqrt{2}} & 0 \\ \frac{i\hbar}{\sqrt{2}} & 0 & \frac{i\hbar}{\sqrt{2}} \\ 0 & -\frac{i\hbar}{\sqrt{2}} & 0 \end{pmatrix} \tag{222}$$

$$[L_2^{'}, L_3^{'}] = \begin{pmatrix} -\frac{i\hbar^2}{2} & 0 & \frac{i\hbar^2}{2} \\ 0 & 0 & 0 \\ -\frac{i\hbar^2}{2} & 0 & \frac{i\hbar^2}{2} \end{pmatrix} - \begin{pmatrix} \frac{i\hbar^2}{2} & 0 & \frac{i\hbar^2}{2} \\ 0 & 0 & 0 \\ -\frac{i\hbar^2}{2} & 0 & -\frac{i\hbar^2}{2} \end{pmatrix} \tag{223}$$

$$[L_2^{'}, L_3^{'}] = i\hbar \begin{pmatrix} -\hbar & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & \hbar \end{pmatrix} = i\hbar L_1' \tag{224}$$

And finally for L_1' and L_3':

$$[L_3', L_1'] = \begin{pmatrix} 0 & \frac{\hbar}{\sqrt{2}} & 0 \\ \frac{\hbar}{\sqrt{2}} & 0 & -\frac{\hbar}{\sqrt{2}} \\ 0 & -\frac{\hbar}{\sqrt{2}} & 0 \end{pmatrix} \begin{pmatrix} -\hbar & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & \hbar \end{pmatrix} - \begin{pmatrix} -\hbar & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & \hbar \end{pmatrix} \begin{pmatrix} 0 & \frac{\hbar}{\sqrt{2}} & 0 \\ \frac{\hbar}{\sqrt{2}} & 0 & -\frac{\hbar}{\sqrt{2}} \\ 0 & -\frac{\hbar}{\sqrt{2}} & 0 \end{pmatrix} \tag{225}$$

$$[L_3^{'}, L_1^{'}] = \begin{pmatrix} 0 & 0 & 0 \\ -\frac{\hbar^2}{\sqrt{2}} & 0 & -\frac{\hbar^2}{\sqrt{2}} \\ 0 & 0 & 0 \end{pmatrix} - \begin{pmatrix} 0 & -\frac{\hbar^2}{\sqrt{2}} & 0 \\ 0 & 0 & 0 \\ 0 & -\frac{\hbar^2}{\sqrt{2}} & 0 \end{pmatrix} \tag{226}$$

$$[L_3^{'}, L_1^{'}] = i\hbar \begin{pmatrix} 0 & -\frac{i\hbar}{\sqrt{2}} & 0 \\ \frac{i\hbar}{\sqrt{2}} & 0 & \frac{i\hbar}{\sqrt{2}} \\ 0 & -\frac{i\hbar}{\sqrt{2}} & 0 \end{pmatrix} = i\hbar L_2' \tag{227}$$

So, these operators are related in the same way as the previous set!

3.6 Summary

These are the steps we have taken to finding the set of matrices that represent the eigenvalues of the angular momentum projection operators in all three directions for certain coordinates.

1) We have to pick L_1, L_2 or L_3 as the pair to L^2.

2) We decided to choose $L_\pm |j,m\rangle = n_{\pm jm} |j, m+1\rangle$ Thus we ended up with one result that satisfies $[L_a, L_b] = i\hbar \mathcal{E}_{abc} L_c$.

3) $u^\dagger L_a u = L_a' \implies [L_a', L_b'] = i\hbar \mathcal{E}_{abc} L_c'$. This results in many other sets of L_a that are equivalent.

4 Changing to spherical to find function solutions

4.1 Rewriting Operators

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Side Note: Matrices for converting between Cartesian and spherical coordinates (will be useful):

$$\begin{pmatrix} dx \\ dy \\ dz \end{pmatrix} = \begin{pmatrix} sin\theta cos\phi & rcos\theta cos\phi & -rsin\theta sin\phi \\ sin\theta sin\phi & rcos\theta sin\phi & rsin\theta cos\phi \\ cos\theta & -rsin\theta & 0 \end{pmatrix} \begin{pmatrix} dr \\ d\theta \\ d\phi \end{pmatrix} \tag{228}$$

$$\begin{pmatrix} dr \\ d\theta \\ d\phi \end{pmatrix} = \begin{pmatrix} sin\theta cos\phi & sin\theta sin\phi & cos\theta \\ \frac{1}{r}cos\theta cos\phi & \frac{1}{r}cos\theta sin\phi & \frac{-1}{r}sin\theta \\ \frac{-sin\phi}{rsin\phi} & \frac{cos\phi}{rsin\theta} & 0 \end{pmatrix} \begin{pmatrix} dx \\ dy \\ dz \end{pmatrix} \tag{229}$$

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Using the matrices above, we can rewrite our operators:

$$\begin{aligned} L_1 &= -i\hbar \left[y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y} \right] \\ &= -i\hbar \left\{ (rsin\theta sin\phi) \left[\cancel{cos\theta \frac{\partial}{\partial r}} - \frac{1}{r}sin\theta \frac{\partial}{\partial \theta} \right] - rcos\theta \left[\cancel{sin\theta sin\phi \frac{\partial}{\partial r}} + \frac{1}{r}cos\theta cos\phi \frac{\partial}{\partial \theta} + \frac{cos\phi}{rsin\theta}\frac{\partial}{\partial \phi} \right] \right\} \\ &= -i\hbar \left\{ (-sin^2\theta sin\phi - cos^2\theta sin\phi)\frac{\partial}{\partial \theta} - cos\phi \frac{cos\theta}{sin\theta}\frac{\partial}{\partial \phi} \right\} \\ &= i\hbar \left[sin\phi \frac{\partial}{\partial \theta} + cos\phi cot\theta \frac{\partial}{\partial \phi} \right] \end{aligned} \tag{230}$$

Similarly, for L_2:

$$L_2 = i\hbar \left[-cos\phi \frac{\partial}{\partial \theta} + sin\phi cot\theta \frac{\partial}{\partial \phi} \right] \tag{231}$$

And for L_3:

$$L_3 = i\hbar \frac{\partial}{\partial \phi} \tag{232}$$

These three angular momentum operators do not derive with respect to r, it becomes clear that:

$$\left[f(r)\frac{\partial}{\partial r}, L_a \right] = 0 \text{ where a=1,2,3} \tag{233}$$

For this reason it might be convenient to rewrite these operators in spherical coordinates. So, for L_+:

$$\begin{aligned} L_+ = L_1 + iL_2 &= \left[i\hbar\left(sin\phi\frac{\partial}{\partial\theta} + cos\phi cot\theta\frac{\partial}{\partial\phi}\right)\right] + i\left[i\hbar\left(-cos\phi\frac{\partial}{\partial\theta} + sin\phi cot\theta\frac{\partial}{\partial\phi}\right)\right] \\ &= \hbar\left[(cos\phi + isin\phi)\frac{\partial}{\partial\theta} + i(cos\phi + isin\phi)cot\theta\frac{\partial}{\partial\phi}\right] \\ &= \hbar\left[(e^{i\phi})\frac{\partial}{\partial\theta} + i(e^{i\phi})cot\theta\frac{\partial}{\partial\phi}\right] \end{aligned} \tag{234}$$

$$L_+ = \hbar e^{i\phi}\left[\frac{\partial}{\partial\theta} + icot\theta\frac{\partial}{\partial\phi}\right] \tag{235}$$

Similarly for L_-:

$$\begin{aligned} L_- = L_1 - iL_2 &= \left[i\hbar\left(sin\phi\frac{\partial}{\partial\theta} + cos\phi cot\theta\frac{\partial}{\partial\phi}\right)\right] - i\left[i\hbar\left(-cos\phi\frac{\partial}{\partial\theta} + sin\phi cot\theta\frac{\partial}{\partial\phi}\right)\right] \\ &= \hbar\left[-(cos\phi + isin\phi)\frac{\partial}{\partial\theta} + i(cos\phi + isin\phi)cot\theta\frac{\partial}{\partial\phi}\right] \\ &= \hbar\left[-(e^{i\phi})\frac{\partial}{\partial\theta} + i(e^{i\phi})cot\theta\frac{\partial}{\partial\phi}\right] \end{aligned} \tag{236}$$

For L_- we could have also used the fact that we previously proved that it's the complex conjugate of L_+.

$$L_- = L_+^\dagger = \hbar e^{-i\phi}\left[-\frac{\partial}{\partial\theta} + icot\theta\frac{\partial}{\partial\phi}\right] \tag{237}$$

4.2 Finding function solutions for integer j's

So far we have just been talking about $|j,m\rangle$ but we can imagine this to include some function Y_{jm} that depends on the angles θ and ϕ

Let's plug this into these following expressions we have derived:

$$L_3|j,m\rangle = \hbar m|j,m\rangle \tag{238}$$

$$L_+|j,m\rangle = \hbar\sqrt{j(j+1) - m^2 - m}\,|j,m+1\rangle \tag{239}$$

$$L_-|j,m\rangle = \hbar\sqrt{j(j+1) - m^2 + m}\,|j,m-1\rangle \tag{240}$$

Plugging in for L_3:

$$L_3|j,m\rangle = \hbar m|j,m\rangle \tag{241}$$

$$-i\hbar\frac{\partial}{\partial\phi}Y_{jm}(\theta,\phi) = \hbar m Y_{jm}(\theta,\phi) \tag{242}$$

$$\implies Y_{jm}(\theta,\phi) = P_j^m(\theta)e^{im\phi} \tag{243}$$

$P_j^m(\theta)$ is the integration constant for $Y_{jm}(\theta,\phi)$. Additionally, we know that ϕ and $\phi + 2\pi$ denote the same angle in these coordinates so:

$$Y_{jm}(\theta,\phi+2\pi) = Y_{jm}(\theta,\phi) \tag{244}$$

$$e^{im(\phi+2\pi)} = e^{im\phi} \implies e^{i2\pi m} = 1 \tag{245}$$

This has the consequence that m values have to be integers. This also means that j at half integers aren't allowed for this particular solution set. However, we know that there should be half integers of this j (if j is a half integer then m must be a half integer), first found out from experiments by Stern and Gerlach. The solutions for these half integers we will find later.

Now plugging in for L_+:

$$L_+ |j,m\rangle = \hbar\sqrt{j(j+1)-m^2-m}\,|j,m+1\rangle \tag{246}$$

$$\hbar e^{i\phi}\left[\frac{\partial}{\partial\theta} + icot\theta\frac{\partial}{\partial\phi}\right]P_j^m(\theta)e^{im\phi} = \hbar\sqrt{j(j+1)-m^2-m}P_j^{m+1}(\theta)e^{i(m+1)\phi} \tag{247}$$

$$\cancel{\hbar e^{i(m+1)\phi}}\left[\frac{\partial}{\partial\theta}P_j^m(\theta) - mcot\theta P_j^m(\theta)\right] = \cancel{\hbar}\sqrt{j(j+1)-m^2-m}P_j^{m+1}(\theta)\cancel{e^{i(m+1)\phi}} \tag{248}$$

$$\implies \left(\frac{\partial}{\partial\theta} - mcot\theta\right)P_j^m(\theta) = \sqrt{j(j+1)-m^2-m}P_j^{m+1}(\theta) \tag{249}$$

This is the recursion relation between the different values of m for each j

Similarly, plugging in for L_- leads to:

$$\implies \left(\frac{\partial}{\partial\theta} + mcot\theta\right)P_j^m(\theta) = -\sqrt{j(j+1)-m^2+m}P_j^{m-1}(\theta) \tag{250}$$

Let's see what happens when m=j and we plug in the first of the above recursion relations:

$$\frac{\partial}{\partial\theta}P_j^j(\theta) - jcot\theta P_j^j(\theta) = 0 \tag{251}$$

Solution is thus:

$$P_j^j(\theta) = N_j[sin\theta]^j \tag{252}$$

Let's check that this makes sense:

$$\frac{\partial P_j^j(\theta)}{\partial\theta} = N_j j[sin\theta]^{j-1}cos\theta = N_j jcot\theta(sin\theta)^j = jcot\theta P_j^j(\theta) \tag{253}$$

Now let's see what happens when we plug in m=-j into the second recursion relation:

$$\frac{\partial}{\partial\theta}P_j^{-j}(\theta) - jcot\theta P_j^{-j}(\theta) = 0 \tag{254}$$

$$\therefore P_j^j = P_j^{-j} = N_j[sin\theta]^j \tag{255}$$

So the solution is of P is the same for both m=-j and m=j.

Now if we want to fix this N (the normalization constant), we follow our typical process of integration and solve for it:

$$1 = \int_0^{2\pi} d\phi \int_0^{\pi} d\theta [Y_{jm}(\theta,\phi)Y_{jm}^*(\theta,\phi)]sin\theta d\theta d\phi \tag{256}$$

4.3 Function solutions for j=1 and m=-1,0,1

Starting with the lowest m-value function, m=-1:

$$P_1^{-1} = Nsin\theta \tag{257}$$

Using recursion relation to find the next value up, m=0:

$$P_1^0 = \frac{\frac{\partial P_1^{-1}}{\partial\theta} + cot\theta Nsin\theta}{\sqrt{2-1+1}} = \frac{Ncos\theta + cot\theta Nsin\theta}{\sqrt{2}} = N\sqrt{2}cos\theta \tag{258}$$

The highest m value should be the same as the lowest (proven above).

Let's normalize $Y_{1,-1}$:

$$\int_0^{2\pi} d\phi \int_0^{\pi} N^2 sin^2\theta \cancel{e^{-i\phi}e^{i\phi}} = 1 \tag{259}$$

$$\implies N = \sqrt{\frac{3}{8\pi}} \tag{260}$$

In conclusion, writing these solutions as $Y_{jm}(\theta,\phi) = P_j^m(\theta)e^{im\phi}$:

$$Y_{1,-1} = \sqrt{\frac{3}{8\pi}}sin\theta e^{-i\phi} \tag{261}$$

$$Y_{1,0} = \sqrt{\frac{3}{8\pi}}\sqrt{2}cos\theta \tag{262}$$

$$Y_{1,1} = \sqrt{\frac{3}{8\pi}}sin\theta e^{i\phi} \tag{263}$$

Using an integral calculator, I confirmed that these functions are all normalized such that $\int_0^{2\pi} d\phi \int_0^{\pi} d_{jm}(\theta,\phi)^* Y_{jm}(\theta,\phi)e^{-im\phi}e^{im\phi} = 1$

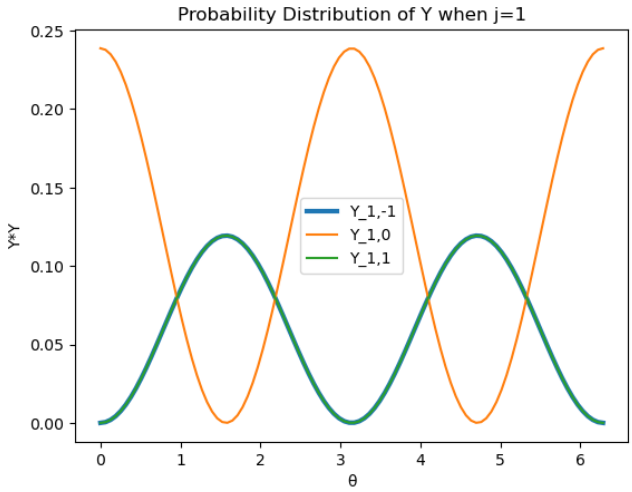
These functions squared such that they become only real are:

$$Y^*_{1,-1}Y_{1,-1} = \frac{3}{8\pi}sin^2\theta \tag{264}$$

$$Y^*_{1,0}Y_{1,0} = \frac{6}{8\pi}cos^2\theta \tag{265}$$

$$Y^*_{1,1}Y_{1,1} = \frac{3}{8\pi}sin^2\theta \tag{266}$$

Plotting these with respect to Y yields:



4.4 Function solutions for j=2 and m=-2,-1,0,1,2

Starting with the lowest m-value function:

$$P_2^{-2} = Nsin^2\theta \tag{267}$$

Using recursion relation to find the next value up:

$$P_2^{-1} = \frac{\frac{\partial P_2^{-2}}{\partial\theta} + 2cot\theta Nsin^2\theta}{\sqrt{6-4+2}} = \frac{2Nsin\theta cos\theta + 2cot\theta Nsin^2\theta}{\sqrt{4}} = 2Ncos\theta sin\theta \tag{268}$$

And the next:

$$P_2^0 = \frac{\frac{\partial P_2^{-1}}{\partial\theta} + cot\theta 2Ncos\theta sin\theta}{\sqrt{6-1+1}} = \frac{2N(-sin^2\theta + cos^2\theta) + cot\theta(2N)cos\theta sin\theta}{\sqrt{6}} = \frac{2}{\sqrt{6}}N(-3sin^2\theta+2) \tag{269}$$

And the next:

$$P_2^0 = \frac{\frac{\partial P_2^0}{\partial \theta} + 0}{\sqrt{6-0-0}} = \frac{\frac{\sqrt{2}}{6}N(-6sin\theta cos\theta)}{\sqrt{6}} = -2Nsin\theta cos\theta \tag{270}$$

The highest m value should be the same as the lowest (proven above).
In conclusion, writing these solutions as $Y_{jm}(\theta,\phi) = P_j^m(\theta)e^{im\phi}$:

$$Y_{2,-2} = Nsin^2\theta e^{-2i\phi} \tag{271}$$

$$Y_{2,-1} = 2Ncos\theta sin\theta e^{-i\phi} \tag{272}$$

$$Y_{2,0} = \frac{2}{\sqrt{6}}N(-3sin^2\theta + 2)e^{2i\phi} \tag{273}$$

$$Y_{2,1} = -2Nsin\theta cos\theta e^{i\phi} \tag{274}$$

$$Y_{2,2} = Nsin^2\theta e^{2i\phi} \tag{275}$$

4.5 Rewriting $\mathbf{L^2}$

Now let's rewrite L^2 in terms of these spherical coordinates. First finding each of the projections (since $L^2 = L_1^2 + L_2^2 + L_3^2$):

$$L_1^2 = -\hbar^2\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right)\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right) = -\hbar^2\left[y^2\frac{\partial^2}{\partial z^2} - y\frac{\partial}{\partial y} - 2yz\frac{\partial^2}{\partial y\partial z} - z\frac{\partial}{\partial z} + z^2\frac{\partial^2}{\partial y^2}\right] \tag{276}$$

$$L_2^2 = -\hbar^2\left(z\frac{\partial}{\partial y} - y\frac{\partial}{\partial z}\right)\left(z\frac{\partial}{\partial y} - y\frac{\partial}{\partial z}\right) = -\hbar^2\left[z^2\frac{\partial^2}{\partial x^2} - z\frac{\partial}{\partial z} - 2zx\frac{\partial^2}{\partial x\partial z} - x\frac{\partial}{\partial x} + x^2\frac{\partial^2}{\partial z^2}\right] \tag{277}$$

$$L_3^2 = -\hbar^2\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right)\left(z\frac{\partial}{\partial y} - y\frac{\partial}{\partial z}\right) = -\hbar^2\left[z^2\frac{\partial^2}{\partial x^2} - z\frac{\partial}{\partial z} - 2zx\frac{\partial^2}{\partial x\partial z} - x\frac{\partial}{\partial x} + x^2\frac{\partial^2}{\partial z^2}\right] \tag{278}$$

Adding these:

$$\begin{aligned} L^2 = -\hbar^2\Bigg[&(x^2+y^2+z^2)\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right) - x^2\frac{\partial^2}{\partial x^2} - y^2\frac{\partial^2}{\partial y^2} + z^2\frac{\partial^2}{\partial z^2} \\ &-2xy\frac{\partial^2}{\partial x\partial y} - 2zx\frac{\partial^2}{\partial z\partial x} - 2yz\frac{\partial^2}{\partial y\partial z} - 2\left(x\frac{\partial}{\partial x} + y\frac{\partial}{\partial y} + z\frac{\partial}{\partial z}\right)\Bigg] \\ = -\hbar^2\left[(x^2+y^2+z^2)(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}) - \left(x\frac{\partial}{\partial x} + y\frac{\partial}{\partial y} + z\frac{\partial}{\partial z}\right)^2 - \left(x\frac{\partial}{\partial x} + y\frac{\partial}{\partial y} + z\frac{\partial}{\partial z}\right)\right] \end{aligned} \tag{279}$$

5 Understanding Total Energy Equation of this System and Comparing to Classical Mechanics

We will work towards an equation for the total energy of this system.

Now let's replace these partial derivatives with their equivalents in spherical coordinates:

$$\left(x\frac{\partial}{\partial x}+y\frac{\partial}{\partial y}+z\frac{\partial}{\partial z}\right)=\left[rsin^2\theta cos^2\phi+rsin^2\theta sin^2\phi+rcos^\theta\right]\frac{\partial}{\partial r} \\ +[sin\theta cos\theta cos^2\phi+sin\theta cos\theta sin^2\phi-sin\theta cos\theta]\frac{\partial}{\partial\theta} \tag{280}$$

$$\implies \frac{-\hbar^2}{2m}\left(x\frac{\partial}{\partial x}+y\frac{\partial}{\partial y}+z\frac{\partial}{\partial z}\right)=\frac{L^2}{2mr^2}-\frac{\hbar^2}{2mr^2}\left[\left(r\frac{\partial}{\partial r}\right)^2+r\frac{\partial}{\partial r}\right] \tag{281}$$

Let's think about this a bit more closely. Left is kinetic energy operator, composed of (right side, first term) angular kinetic energy operator and (right side, second term) radial kinetic energy operator.

So, total energy H includes this operator plus a potential energy operator (which must only depend on r):

$$H=\frac{L^2}{2mr^2}-\frac{\hbar^2}{2mr^2}\left[(r\frac{\partial}{\partial r})^2+r\frac{\partial}{\partial r}\right]+V(r) \tag{282}$$

$$[f(r)\frac{\partial}{\partial r},L_a]=0 \tag{283}$$

So now we have three commuting operator and can simultaneously diagonalize all three: H,L, and L_3

Once more so we don't forget, these are the three operators:

$$L_3\left|E,j,m\right\rangle=\hbar m\left|E,j,m\right\rangle \tag{284}$$

$$L^2\left|E,j,m\right\rangle=\hbar^2 j(j+1)\left|E,j,m\right\rangle \tag{285}$$

$$H\left|E,j,m\right\rangle=E\left|E,j,m\right\rangle \tag{286}$$

Looking at H:

$$\left\{\frac{-\hbar^2}{2mr^2}\left[\left(r\frac{\partial}{\partial r}\right)^2+\left(r\frac{\partial}{\partial r}\right)\right]+V(r)+\frac{\hbar^2 j(j+1)}{2mr^2}\right\}\left|E,j,m\right\rangle=E\left|E,j,m\right\rangle \tag{287}$$

But what is this $|E,j,m\rangle$? It is some function:

$$\psi_{E,j,m}(r,\theta,\phi)=R_{E,j}(r)Y_{j,m}(\theta,\phi) \tag{288}$$

Where $R_{E,j}(r)$ is simply an integration constant. Note that we did not use separation of variables.

Therefore, rewriting again:

$$\left\{\frac{-\hbar^2}{2mr^2}\left[\left(r\frac{\partial}{\partial r}\right)^2+\left(r\frac{\partial}{\partial r}\right)-j(j+1)\right]+V(r)-E\right\}|E,j,m\rangle=0 \tag{289}$$

We might recall from classical mechanics central force problem:

$$\frac{1}{2}m\left(\frac{d\rho}{dt}\right)^2+\frac{L^2}{2m\rho^2}+V(\rho)-E=0 \tag{290}$$

Comparing these two, we notice that the angular kinetic energy term is $\frac{L^2}{2m\rho^2}$ in classical and $\frac{\hbar^2 j(j+1)}{2mr^2}$ in quantum. The quantization of the angular kinetic energy is apparent given that j are only certain values.

Now, we will denote:

$$R_{E,j}=\frac{U_{E,j}(r)}{r} \tag{291}$$

Meaning that:

$$\left[\left(r\frac{\partial}{\partial r}\right)^2+r\frac{\partial}{\partial r}\right]R_{E,j}(r)=\frac{r\partial^2 U_{E,j}(r)}{\partial r^2} \tag{292}$$

Plugging this into total expression:

$$\frac{-\hbar^2}{2mr^2}\left[r^2\frac{d^2U_{E,j}(r)}{dr^2}-j(j+1)\frac{U_{E,j}(r)}{r}\right]+V(r)\frac{U_{E,j}(r)}{r}-E\frac{U_{E,j}(r)}{r}=0 \tag{293}$$

$$\implies \frac{d^2U_{E,j}(r)}{dr^2}+\frac{2m}{\hbar}\left(E-V(r)-\frac{\hbar^2}{2m}\frac{j(j+1)}{r^2}\right)U_{E,j}(r)=0 \tag{294}$$

This $E-V(r)-\frac{\hbar^2}{2m}\frac{j(j+1)}{r^2}$ looks like the term from classical mechanics that was crucial for analysis of the central force problem, $\frac{L^2}{2m\rho^2}+V(\rho)-E$.

6 Continuing to improve the form of our wave function

Overall we discovered that the wave function looks like:

$$\psi_{E,j,m}(r,\theta,\phi)=R_{E,j}(r)Y_{j,m}(\theta,\phi)=\frac{U_{E,j}(r)}{r}P_j^m(\theta)e^{im\phi} \tag{295}$$

Additionally, the probability function looks like:

$$P(r,\theta,\phi) = \frac{U_{E,j}^2(r)}{r^2}\left[P_j^m(\theta)\right]^2 \tag{296}$$

In order to normalize:

$$1 = \int_0^\infty dr \int_0^\pi d\theta \int_0^{2\pi} d\phi(r^2 sin\theta) P(r,\theta,\phi) = 2\pi \left(\int_0^\infty dr U_{E,j}^2(r)\right)\left(\int_0^\pi d\theta \left[P_j^m(\theta)\right]^2 sin\theta\right) \tag{297}$$

Therefore $\int_0^\infty U_{E,j}^2 dr$ must be finite and $U_{E,j}^2 \to 0$ as $r \to \infty$.
When $r \to 0$, $U_{E,j}(r) \to r^P$

$$\int_0^\epsilon r^{2P} dr = \frac{r^{2P+1}}{2P+1}|_0^\epsilon \tag{298}$$

$$\therefore 2P+1 > 0 \implies P > \frac{-1}{2} \tag{299}$$

When r is small:

$$0 = P(P-1)r^{P-2} - j(j+1)r^{P-2} + \frac{2m}{\hbar^2}(E - V(r))r^P \tag{300}$$

When r is close to 0, the last term can be ignored.

$$\implies V(r)r^P < r^{P-2} \tag{301}$$

$$V(r) < \frac{1}{r^2} \tag{302}$$

$$\implies P(P-1)r^{P-2} = j(j+1)r^{P-2} \implies P(P-1) = j+1, -j \tag{303}$$

r^{-j} only works for j=0. We will assume V(r) has no delta function terms, thus ruling $-j$ out.

What if $j = 0$, $m = 0$, and $P_0^0 = 1$? What is the kinetic energy for this? Well our kinetic energy expression is:

$$\frac{-\hbar^2}{2m}\left[\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right]\frac{1}{r} = \vec{\nabla}\cdot(\vec{\nabla}\frac{1}{r}) \propto \delta(x-0), \delta(y-0), \delta(z-0) \tag{304}$$

$$R_{E,j}(r) = \frac{U_{E,j}(r)}{r} = r^j w_{e_j}(r) \tag{305}$$

$$U_{E,j} \to 0 \text{ as } r \to \infty \tag{306}$$

$$U_{E,j}(r) \approx r^{j+1} \text{ as } r \to \infty \tag{307}$$

$$P(P-1) = j(j+1) \implies P = -j \text{ and } P = j+1 \tag{308}$$

$$P > \frac{1}{2} \tag{309}$$

Change of variable:

$$U_{E,j}(r) = r^{j+1} w_{E,j}(r) \tag{310}$$

$$\frac{dU_{E,j}}{dr} = (j+1) r^j w_{E,j} + r^{j+1} \frac{dw_{E,j}(r)}{dr} \tag{311}$$

$$\frac{d^2 U_{E,j}}{dr^2} = (j+1) j r^{j-1} w_{E,j}(r) + 2(j+1) r^j \frac{dw_{E,j}(r)}{dr} + r^{j+1} \frac{d^2 w_{E,j}(r)}{dr^2} \tag{312}$$

Plug these in:

$$j(j+1) r^{j-1} w_{E,j}(r) + \frac{2m}{\hbar^2} [E - V(r)] r^{j+1} w_{E,j}(r) + \frac{2(j+1) r^j dw_{E,j}(r)}{dr} - j(j+1) r^{j-1} w_{E,j}(r) + r^{j+1} \frac{d^2 w_{E,j}(r)}{dr^2} = 0 \tag{313}$$

$$\implies \frac{d^2 w_{E,j}(r)}{dr^2} + \frac{2(j+1)}{r} \frac{dw_{E,j}(r)}{dr} + \frac{2m}{\hbar^2} [E - V(r)] w_{E,j}(r) = 0 \tag{314}$$

Quantum Mechanics- Part 6

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Contents

1 Hydrogen Atom

1.1 Hydrogenic Atom Potential

A hydrogenic atom has the following potential:

$$V(r) = \frac{-1}{4\pi\epsilon_0}\frac{Ze^2}{r} \tag{1}$$

Where ϵ_0 is the permitivity of free space, Z is the atomic number (1 in the case of hydrogen), and e is the charge of an electron

We will do the substitution $r = bu$ where b is some unit of length.

Instead of using our $w_{E,j}(r)$ function, we define:

$$w_{E,j}(bu) \equiv \chi_{E,j}(u) \tag{2}$$

Now we can rewrite our energy equation as:

$$\frac{1}{b^2}\frac{d^2\chi_{E,j}(u)}{du^2} + \frac{2(j+1)}{b^2u}\frac{d\chi_{E,j}(u)}{du} + \left(\frac{2m}{\hbar^2}E + \frac{2m}{\hbar^2}\frac{Ze^2}{4\pi\epsilon_0}\frac{1}{bu}\right)\chi_{E,j}(u) = 0 \tag{3}$$

We multiply this by b^2:

$$\frac{d^2\chi_{E,j}(u)}{du^2} + \frac{2(j+1)}{u}\frac{d\chi_{E,j}(u)}{du} + \left(\frac{2mb^2}{\hbar^2}E + \frac{2m}{\hbar^2}\frac{Ze^2}{4\pi\epsilon_0}\frac{b}{u}\right)\chi_{E,j}(u) = 0 \tag{4}$$

We will also set:

$$\frac{2m}{\hbar^2}\frac{Ze^2}{4\pi\epsilon_0}b = 1 \tag{5}$$

And by plugging in all these constants and rearranging for b we arrive at:

$$b = \frac{1}{Z}2.64588603 \times 10^{-11} \text{ meters} \tag{6}$$

Looking at the other term in equation 4 we see that the units of $\frac{2mb^2}{\hbar^2}$ are Joules, meaning for natural units of energy we can set:

$$E = \frac{-\hbar}{2mb^2}\beta^2 \tag{7}$$

So, rewriting equation 4:

$$\frac{d^2\chi_{E,j}(u)}{du^2} + \frac{2(j+1)}{u}\frac{d\chi_{E,j}(u)}{du} - \beta^2\chi_{E,j}(u) + \frac{1}{u}\chi_{E,j}(u) = 0 \tag{8}$$

1.2 As u approaches infinity

As $u \to \infty$, this equation becomes:

$$\frac{d^2\chi_{E,j}(u)}{du^2} \sim \alpha\chi_{E,j}(u) \tag{9}$$

This implies that as $u \to \infty$:

$$\chi_{E,j}(u) \sim e^{-\beta u} \tag{10}$$

Therefore, the total solution will thus be in this form:

$$\chi_{E,j}(u) = e^{-\beta u}R_{E,j}(u) \tag{11}$$

We can take derivatives of this:

$$\frac{d\chi_{E,j}(u)}{du} = -\beta e^{-betau}R_{E,j}(u) + e^{-\beta u}\frac{dR_{E,j}(u)}{du} \tag{12}$$

$$\frac{d^2\chi_{E,j}(u)}{du^2} = \beta^2 e^{-\beta u}R_{E,j}(u) - 2\beta e^{-\beta u}\frac{dR_{E,j}(u)}{du} + e^{-\beta u}\frac{d^2R_{E,j}(u)}{du^2} \tag{13}$$

And use these to plug back into equation 8, resulting in:

$$u\frac{d^2R_{E,j}(u)}{du^2} + (2(j+1) - 2\beta u)\frac{dR_{E,j}(u)}{du} + (1 - 2(j+1)\beta)R_{E,j}(u) = 0 \tag{14}$$

Now we take this $R_{E,j}(u)$ and rewrite it as a polynomial which we know would have this form.:

$$R_{E,j}(u) = \sum_{k=0}^{\infty} c_k u^k \tag{15}$$

The first and second derivatives are:

$$\frac{dR_{E,j}(u)}{du} = \sum_{k=0}^{\infty}(k+1)c_{k+1}u^k \tag{16}$$

$$\frac{d^2R_{E,j}(u)}{du^2} = \sum_{k=0}^{\infty}(k+1)(k+2)c_{k+2}u^k \tag{17}$$

So, using these to plug back into equation 14 results in:

$$\sum_{k=0}^{\infty}\{[2(j+1)(k+1) + k(k+1)]c_{k+1} + [(-2\beta)k + (1 - 2(j+1)\beta)]c_k\}u^k = 0 \tag{18}$$

Since each of these terms in the sum must be 0 in order for the total sum to be 0, we know that the coefficient of each term must be 0:

$$[2(j+1)(k+1) + k(k+1)]c_{k+1} + [(-2\beta)k + (1 - 2(j+1)\beta)]c_k = 0 \tag{19}$$

$$\implies C_{k+1} = \frac{2\beta(k+j+1)-1}{k(k+1)+2(j+1)(k+1)} \tag{20}$$

This is our "recursion relation."

Furthermore Going back to our definition in equation 11, we know that this polynomial $R_{E,j}(u)$ must terminate because $\chi_{E,j} \to 0$ as $u \to \infty$ (due to normalizability conditions):

$$\lim_{u\to\infty} \frac{u^k}{e^{\beta u}} = 0 \tag{21}$$

This means that in the sum in equation 18, we must reach a point where the term is zero (because the polynomial must terminate, and for this to happen, there must be some P for which:

$$2\beta(j+P+1)-1 = 0 \tag{22}$$

We can rearrange for a value of β:

$$\beta = \frac{1}{2(j+P+1)} = \frac{1}{2n} \tag{23}$$

So, our solutions depend on 4 quantum numbers:

$$\begin{aligned} &n = 1, 2, 3, ... \\ &P = 0, 1, 2, ... \\ &j = 0, 1, 2, ... \\ &m = -j, -j+1, .., j \end{aligned} \tag{24}$$

And the energy and natural unit b look like:

$$b = \frac{2\pi\epsilon_0\hbar^2}{Ze^2m} \tag{25}$$

$$E = \frac{-\hbar^2}{2mb^2} = \frac{-Z^2e^4m}{8\pi^2\epsilon_0^2\hbar^2}\beta^2 = \frac{-Z^2e^4m}{32\pi^2\epsilon_0^2\hbar^2n^2} \tag{26}$$

And, the total wave function, with all the changes of variable we have made will look like:

$$\psi_{n,j,m}(bu,\theta,\phi) = \left(\sum_{k=0}^{\infty} c_k u^k\right) e^{-\beta u}(bu)^j P_j^m e^{im\phi} \tag{27}$$

where $\beta = \frac{1}{2n}$

2 Hydrogen Energy Levels and States

We can rewrite the above expression to be in terms of r once more:

$$\psi_{n,j,m}(r,\theta,\phi) = \left(\sum_{k=0}^{\infty} c_k \left(\frac{r}{b}\right)^k\right) e^{-\frac{r}{2bn}} r^j P_j^m e^{im\phi} \tag{28}$$

Where P is the upper limit of k and $P = n - j - 1$

In order to find the normalization constant we integrate over the entire volume, set this integral to 1, and solve for N:

$$1 = N^2 \int_0^{\infty} \int_0^{2\pi} \int_0^{\pi} \psi^* \psi dr d\theta d\phi \tag{29}$$

2.1 n=1 Wave Functions

$$\underline{j = 0, m = 0}$$

$$\psi_{100} = \sqrt{\frac{1}{8\pi b^3}} e^{\frac{-r}{2b}} \tag{30}$$

2.2 n=2 Wave Functions

$$\underline{j = 0, m = 0}$$

$$\psi_{200} = \sqrt{\frac{1}{64\pi b^3}} \left(\frac{-r}{4b} + 1\right) e^{\frac{-r}{4b}} \tag{31}$$

$$\underline{j = 1, m = -1}$$

$$\psi_{21-1} = \sqrt{\frac{1}{2048\pi b^5}} r e^{\frac{-r}{4b}} sin\theta e^{-i\phi} \tag{32}$$

$$\underline{j = 1, m = 0}$$

$$\psi_{210} = \sqrt{\frac{1}{2048\pi b^5}} \sqrt{2} r e^{\frac{-r}{4b}} cos\theta \tag{33}$$

$$\underline{j = 1, m = 1}$$

$$\psi_{211} = \sqrt{\frac{1}{2048\pi b^5}} r e^{\frac{-r}{4b}} sin\theta e^{i\phi} \tag{34}$$

2.3 n=3

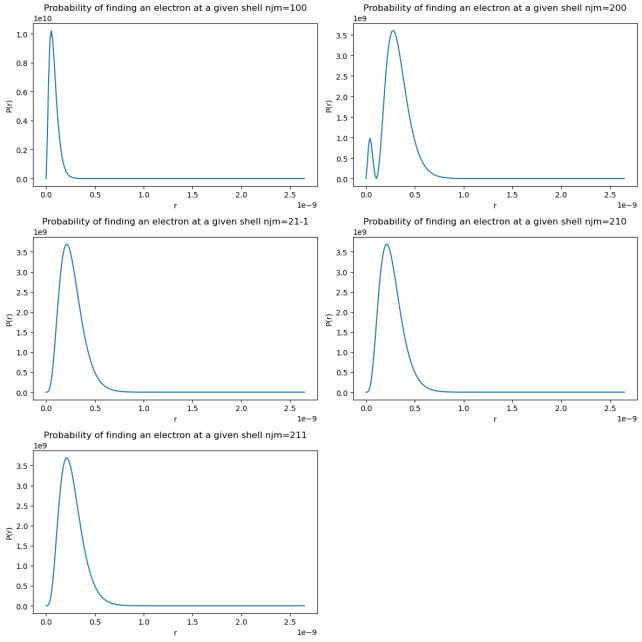
$$
\begin{aligned}
&n = 3: \\
&P = 0, j = 2, m = -2, -1, 0, 1, 2 \\
&P = 1, j = 1, m = -1, 0, 1 \\
&P = 2, j = 0, m = 0
\end{aligned}
\tag{35}
$$

In a given energy level (value of n), are all the states orthogonal to each other?

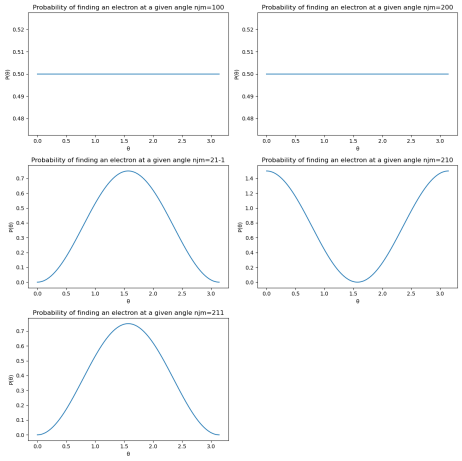
Yes, because orthogonality is independent for r, θ, ϕ. Since either P's,j's, or m's are different for each state, they're all orthogonal

2.4 Analysis

By integrating with respect to $d\theta$ and $d\phi$ with trespect their area we can find the probability of finding the particle on the surface of an infinitesimal sphere:



We can also integrate with respect to dr and $d\phi$ to find the probability density of finding the particle at a given angle θ:



3 Effect of Temperature on energy states

3.1 Atom

Starting at a temperature arbitrarily close to zero, what temperature would you need to raise an atom or group of atoms to in order to have electrons exist in the next state up?

Thanks to Boltzmann we know that:

$$\frac{P_{n+1}}{P_n} = e^{\frac{-1}{k_B T}(E_{n+1} - E_n)} \tag{36}$$

$$P(n) \propto e^{\frac{-1}{k_B T} E_n} \tag{37}$$

Where $P(n)$ is the probability of a given n.

When an electron changes state and loses or gains energy, this can be due to either the transfer of heat or of light, meaning:

$$E_{n+1} - E_n = \hbar\omega = k_B T \tag{38}$$

4 Relativistic Energy Operator

4.1 Introduction to the problem (What if j is not an integer?)

We recall that:

$$E = \frac{p^2}{2m} = i\hbar\frac{\partial}{\partial t} \tag{39}$$

$$\vec{p} = -i\hbar\nabla \tag{40}$$

We also might recall from any modern physics class that $E^2 = p^2c^2 + m^2c^4$. In my modern physics class we never wrote $E = \sqrt{p^2c^2 + m^2c^4}$ because $E \geq 0$.

In order to get it in a better form we write:

$$E = mc^2\sqrt{1 + \frac{p^2}{m^2c^2}} = mc^2(1 + \frac{p^2}{2mc^2} + ...) = mc^2 + \frac{p^2}{2m} \tag{41}$$

This becomes

$$E - mc^2 = \frac{p^2}{2m} \tag{42}$$

Our goal now is to find an operator to represent this relativistic energy. The first idea that physicists Klein and Gordon had was to find an E^2 operator:

$$\left[-\hbar^2\frac{\partial}{\partial t^2} = -\hbar^2c^2\frac{\partial}{\partial x^2} + m^2c^4\right]\psi(x,t) \tag{43}$$

However in this case we find that $\psi^*\psi \neq P$. Instead you can do $i(\psi^*\frac{\partial\psi}{\partial t} - \psi\frac{\partial\psi}{\partial t})$ but the issue is that this is not real AND positive.

Dirac was more ambitious. He proposed actually finding the square root of this:

$$\left(\sqrt{-\hbar^2c^2\frac{\partial^2}{\partial x^2}}\right)\psi(x,t) = i\hbar\frac{\partial}{\partial t}\psi(x,t) \tag{44}$$

Let's try to rewrite this operator in a better form, such as (where α and β are some constants):

$$\begin{gathered}(\alpha\frac{\partial}{\partial x} + \beta)^2 = -\hbar^2c^2\frac{\partial^2}{\partial x^2} + m^2c^4 \\ = \alpha^2\frac{\partial^2}{\partial x^2} + \beta^2 + \alpha\beta\frac{\partial}{\partial x} + \beta\alpha\frac{\partial}{\partial x} + \alpha\left(\frac{\partial\alpha}{\partial x}\right)\frac{\partial}{\partial x} + \alpha\frac{\partial\beta}{\partial x}\end{gathered} \tag{45}$$

In order to find the value of α and β we will first take a detour back to discussing our angular momentum operators, which as we recall include:

$$L^2\left|jm\right\rangle = \hbar^2j(j+1)\left|jm\right\rangle \tag{46}$$

$$L_3\left|jm\right\rangle = \hbar m\left|jm\right\rangle \tag{47}$$

$$L_+\left|jm\right\rangle = \hbar\sqrt{j(j+1) - m^2 - m}\left|j, m+1\right\rangle \tag{48}$$

$$L_-\left|jm\right\rangle = \hbar\sqrt{j(j+1) - m^2 + m}\left|j, m-1\right\rangle \tag{49}$$

As you might remember, we argued that solution of $j = \frac{1}{2}(m = \frac{-1}{2}, \frac{1}{2})$ weren't physically relevant because they have the consequence that $e^{im(\phi+2\pi)} \neq e^{im\phi}$.

Nonetheless, just for fun, let's look at the solutions to the angular momentum operators for $j = \frac{1}{2}$ and see what happens:

$$L^2 |\frac{1}{2}, \pm\frac{1}{2}\rangle = \frac{3}{4}\hbar^2 |\frac{1}{2}, \pm\rangle \tag{50}$$

$$L_3 |\frac{1}{2}, \frac{1}{2}\rangle = \frac{\hbar}{2} |\frac{1}{2}, \frac{1}{2}\rangle \tag{51}$$

$$L_3 |\frac{1}{2}, \frac{-1}{2}\rangle = \frac{-\hbar}{2} |\frac{1}{2}, \frac{-1}{2}\rangle \tag{52}$$

$$L_+ |\frac{1}{2}, \frac{-1}{2}\rangle = \hbar\sqrt{\frac{3}{4} - \frac{1}{4} + \frac{1}{2}} |\frac{1}{2}, \frac{1}{2}\rangle = \hbar |\frac{1}{2}, \frac{1}{2}\rangle \tag{53}$$

$$L_- |\frac{1}{2}, \frac{1}{2}\rangle = \hbar |\frac{1}{2}, \frac{-1}{2}\rangle \tag{54}$$

Now we can write the expectation value of these operators in the form of the matrix such that for L_3 for example: $(L_3)_{m_1 m_2} = \langle j_1, m_1 | L_3 | j_2, m_2 \rangle$

So for these operators for $j = \frac{1}{2}$:

$$(L_+)_{m_1 m_2} = \begin{pmatrix} 0 & 0 \\ \hbar & 0 \end{pmatrix} \tag{55}$$

$$(L_-)_{m_1 m_2} = \begin{pmatrix} 0 & \hbar \\ 0 & 0 \end{pmatrix} \tag{56}$$

$$(L_1)_{m_1 m_2} = \begin{pmatrix} 0 & \frac{\hbar}{2} \\ \frac{\hbar}{2} & 0 \end{pmatrix} = \frac{\hbar}{2} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} = \frac{\hbar}{2}\sigma_1 \tag{57}$$

$$(L_2)_{m_1 m_2} = \begin{pmatrix} 0 & \frac{\hbar}{2} \\ \frac{-i\hbar}{2} & 0 \end{pmatrix} = \frac{\hbar}{2} \begin{pmatrix} 0 & i \\ -i & 0 \end{pmatrix} = \frac{\hbar}{2}\sigma_2 \tag{58}$$

$$(L_3)_{m_1 m_2} = \begin{pmatrix} \frac{-\hbar}{2} & 0 \\ 0 & \frac{\hbar}{2} \end{pmatrix} = \frac{\hbar}{2} \begin{pmatrix} -1 & 0 \\ 0 & 1 \end{pmatrix} = \frac{\hbar}{2}\sigma_3 \tag{59}$$

*L_1 and L_2 are found by remembering $L_1 = \frac{L_+ + L_-}{2}$ and $L_2 = \frac{L_+ - L_-}{2}$

Based on this information, we can rewrite this equation from earlier too by defining $L_a = \frac{\hbar}{2}\sigma_a$. These σ matrices are called Paul matrices.:

$$[L_a, L_b] = i\hbar\mathcal{E}_{abc}L_c \tag{60}$$

$$\implies \frac{\hbar^2}{4}[\sigma_a, \sigma_b] = \frac{i\hbar^2}{2}\mathcal{E}_{abc}\sigma_c \tag{61}$$

$$\implies [\sigma_a, \sigma_b] = 2i\mathcal{E}_{abc}\sigma_c \tag{62}$$

What are the properties of these Paul matrices and do they commute?

$$\sigma_1^2 = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}^2 = \mathbb{1} \tag{63}$$

$$\sigma_2^2 = \begin{pmatrix} 0 & i \\ -i & 0 \end{pmatrix}^2 = \mathbb{1} \tag{64}$$

$$\sigma_3^2 = \begin{pmatrix} -1 & 0 \\ 0 & 1 \end{pmatrix}^2 = \mathbb{1} \tag{65}$$

$$\sigma_1\sigma_2 = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}\begin{pmatrix} 0 & i \\ -i & 0 \end{pmatrix} = \begin{pmatrix} -i & 0 \\ 0 & i \end{pmatrix} = i\begin{pmatrix} -1 & 0 \\ 0 & 1 \end{pmatrix} = i\sigma_3 \tag{66}$$

Therefore, from (57) we know:

$$\sigma_2\sigma_1 = -i\sigma_3 \tag{67}$$

Similarly:

$$\sigma_2\sigma_3 = \begin{pmatrix} 0 & i \\ -i & 0 \end{pmatrix}\begin{pmatrix} -1 & 0 \\ 0 & 1 \end{pmatrix} = \begin{pmatrix} 0 & i \\ i & 0 \end{pmatrix} = i\sigma_1 \tag{68}$$

$$\sigma_3\sigma_2 = -i\sigma_1 \tag{69}$$

And:

$$\sigma_3\sigma_1 = \begin{pmatrix} -1 & 0 \\ 0 & 1 \end{pmatrix}\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} = i\begin{pmatrix} 0 & i \\ -i & 0 \end{pmatrix} = i\sigma_2 \tag{70}$$

$$\sigma_1\sigma_3 = -i\sigma_2 \tag{71}$$

Therefore, this can be summarized through what we call "anti-commutators":

$$\sigma_1\sigma_2 + \sigma_2\sigma_1 = 0 \tag{72}$$

$$\sigma_2\sigma_3 + \sigma_3\sigma_2 = 0 \tag{73}$$

$$\sigma_1\sigma_3 + \sigma_3\sigma_1 = 0 \tag{74}$$

Alternatively it can be summarized like this:

$$\sigma_a\sigma_b = i\mathcal{E}_{abc}\sigma_c + \delta_{ab}\mathbb{1} \tag{75}$$

This was all for the special case of $j = \frac{1}{2}$.

Now this below is a Clifford algebra, the answer to which generalizes what we're going to work on into more dimensions:

$$\{\gamma_a, \gamma_b\} = 2\delta_{ab} \tag{76}$$

4.2 1 spacial dimension and 1 time dimension

To solve for our relativisitic energy operator we will start solving with one dimension of space and one of time. The squared operator would thus look like:

$$(\not{D})^2 = -\hbar^2\frac{\partial^2}{\partial t^2} + \hbar^2c^2\frac{\partial^2}{\partial x^2} \tag{77}$$

*By the way, this slashed D, $\not{D}$, is used in honor of Dirac.

We will try to solve for the non-squared operator by writing it in this form and solving for γ_0 and γ_1:

$$\not{D} = i\hbar\gamma_0\frac{\partial}{\partial t} - i\hbar c\gamma_1\frac{\partial}{\partial x} \tag{78}$$

So, the squared operator would look like:

$$\not{D} = (i\hbar\gamma_0\frac{\partial}{\partial t} - i\hbar c\gamma_1\frac{\partial}{\partial x})(i\hbar\gamma_0\frac{\partial}{\partial t} - i\hbar c\gamma_1\frac{\partial}{\partial x}) = \hbar^2\gamma_0\frac{\partial^2}{\partial t^2} - \hbar^2c^2\gamma_1^2\frac{\partial^2}{\partial x^2} + \hbar^2c(\gamma_1\gamma_0 + \gamma_0\gamma_1)\frac{\partial^2}{\partial t\partial x} \tag{79}$$

Therefore, to satisfy (72) we know the following must be true

$$\gamma_0^2 = 1,\ \gamma_1^2 = -1,\ \gamma_1\gamma_0 + \gamma_0\gamma_1 = 0 \tag{80}$$

Dirac had the idea of using:

$$\gamma_0 = \sigma_0,\ \gamma_1 = i\sigma_2 \tag{81}$$

Using this, $\not{D}$ becomes :

$$\not{D} = i\hbar\begin{pmatrix}0 & 1\\ 1 & 0\end{pmatrix}\frac{\partial}{\partial t} + \hbar c\begin{pmatrix}0 & 1\\ -1 & 0\end{pmatrix}\frac{\partial}{\partial x} = \begin{pmatrix}0 & i\hbar\frac{\partial}{\partial t} + i\hbar c\frac{\partial}{\partial x}\\ i\hbar\frac{\partial}{\partial t} - i\hbar c\frac{\partial}{\partial x} & 0\end{pmatrix} \tag{82}$$

4.3 2 Dimensions of Space and 1 of Time

Having understood one dimension of space, we can add a second to the solution by adding another partial derivative to our squared operator:

$$(\not{D})^2 = -\hbar^2\frac{\partial^2}{\partial t^2} + \hbar^2c^2\frac{\partial^2}{\partial x^2} + \hbar^2c^2\frac{\partial^2}{\partial y^2} \tag{83}$$

$$\not{D} = i\hbar\gamma_0\frac{\partial}{\partial t} - i\hbar c\gamma_1\frac{\partial}{\partial x} - i\hbar c\gamma_2\frac{\partial}{\partial y} \tag{84}$$

$$(\not{D})^2 = -\hbar^2\gamma_0^2\frac{\partial}{\partial t^2} - \hbar^2c^2\gamma_1^2\frac{\partial}{\partial x^2} + \hbar^2c(\gamma_1\gamma_0 + \gamma_0\gamma_1)\frac{\partial^2}{\partial t\partial x} + \hbar^2c(\gamma_2\gamma_0 + \gamma_0\gamma_2)\frac{\partial^2}{\partial t\partial y} - \hbar^2c^2(\gamma_1\gamma_2 + \gamma_2\gamma_1)\frac{\partial^2}{\partial x\partial y} - \hbar^2c^2\gamma_2\frac{\partial}{\partial} \tag{85}$$

Therefore, the conditions of a solution of this form are:

$$\begin{gathered}\gamma_0^2 = 1,\ \gamma_1^2 = -1,\ \gamma_2^2 = -1,\\ \gamma_1\gamma_0 + \gamma_0\gamma_1 = 0,\ \gamma_2\gamma_0 + \gamma_0\gamma_2 = 0,\ \gamma_1\gamma_2 + \gamma_2\gamma_1 = 0\end{gathered} \tag{86}$$

Like before, we can use our Pauli matrices as solutions:

$$\gamma_0 = \sigma_1,\ \gamma_1 = i\sigma_2,\ \gamma_2 = i\sigma_3 \tag{87}$$

Therefore the total operator solution is:

$$\not{D} = i\hbar\begin{pmatrix}0 & 1\\ 1 & 0\end{pmatrix}\frac{\partial}{\partial t} + \hbar c\begin{pmatrix}0 & i\\ -i & 0\end{pmatrix}\frac{\partial}{\partial x} + \hbar c\begin{pmatrix}-1 & 0\\ 0 & 1\end{pmatrix}\frac{\partial}{\partial y} = \begin{pmatrix}-\hbar c\frac{\partial}{\partial y} & i\hbar\frac{\partial}{\partial t} + i\hbar c\frac{\partial}{\partial x}\\ i\hbar\frac{\partial}{\partial t} - i\hbar c\frac{\partial}{\partial x} & \hbar c\frac{\partial}{\partial y}\end{pmatrix} \tag{88}$$

4.4 3 Dimensions of Space and 1 of Time

Finally, we extend this to the z dimension. The operator thus looks like:

$$(\not{D})^2 = -\hbar^2\frac{\partial^2}{\partial t^2} + \hbar^2c^2\frac{\partial^2}{\partial x^2} + \hbar^2c^2\frac{\partial^2}{\partial y^2} + \hbar^2c^2\frac{\partial^2}{\partial z^2} \tag{89}$$

$$\not{D} = i\hbar\gamma_0\frac{\partial}{\partial t} - i\hbar c\gamma_1\frac{\partial}{\partial x} - i\hbar c\gamma_2\frac{\partial}{\partial y} - i\hbar c\gamma_3\frac{\partial}{\partial z} \tag{90}$$

$$\begin{aligned}(\not{D})^2 = -\hbar^2\gamma_0^2\frac{\partial}{\partial t^2} - \hbar^2c^2\gamma_1^2\frac{\partial}{\partial x^2} + \hbar^2c(\gamma_1\gamma_0+\gamma_0\gamma_1)\frac{\partial^2}{\partial t\partial x} + \hbar^2c(\gamma_2\gamma_0+\gamma_0\gamma_2)\frac{\partial^2}{\partial t\partial y}\\ -\hbar^2c^2(\gamma_1\gamma_2+\gamma_2\gamma_1)\frac{\partial^2}{\partial x\partial y} - \hbar^2c^2\gamma_2\frac{\partial^2}{\partial y^2} - \hbar^2c^2\gamma_3^2\frac{\partial^2}{\partial z^2} + \hbar^2c^2(\gamma_3\gamma_0+\gamma_0\gamma_3)\frac{\partial^2}{\partial t\partial z}\\ -\hbar^2c^2(\gamma_1\gamma_3+\gamma_3\gamma_1)\frac{\partial^2}{\partial x\partial z} - \hbar^2c^2(\gamma_2\gamma_3+\gamma_3\gamma_2)\frac{\partial^2}{\partial y\partial z}\end{aligned} \tag{91}$$

Therefore, the conditions of a solution of this form are:

$$\begin{gathered}\gamma_0^2 = 1,\ \gamma_1^2 = -1,\ \gamma_2^2 = -1,\ \gamma_3^2 = -1\\ \gamma_1\gamma_0+\gamma_0\gamma_1 = 0,\ \gamma_2\gamma_0+\gamma_0\gamma_2 = 0,\ \gamma_1\gamma_2+\gamma_2\gamma_1 = 0,\ \gamma_3\gamma_0+\gamma_0\gamma_3 = 0\end{gathered} \tag{92}$$

Now, unlike before, we cannot just use the Pauli matrices for our solutions because there is only 3. Rather we will extend the matrices to be 4×4 matrices such that:

$$\gamma_{0_{4\times4}} = \begin{pmatrix}\mathbb{1}_{2\times2} & 0\\ 0 & -\mathbb{1}_{2\times2}\end{pmatrix} \tag{93}$$

$$\gamma_{i_{4\times4}} = \begin{pmatrix}0 & -\sigma_i\\ \sigma_i & 0\end{pmatrix},\ i = 1,2,3 \tag{94}$$

Don't forget that these Pauli matrices are specific to $j = \frac{1}{2}$ and are as follows:

$$\sigma_1 = \begin{pmatrix}0 & 1\\ 1 & 0\end{pmatrix} \tag{95}$$

$$\sigma_2 = \begin{pmatrix}0 & i\\ -i & 0\end{pmatrix} \tag{96}$$

$$\sigma_3 = \begin{pmatrix}-1 & 0\\ 0 & 1\end{pmatrix} \tag{97}$$

Squaring our γ matrices to find what some of the conditions look like:

$$\gamma_0^2 = \mathbb{1} \tag{98}$$

$$\gamma_i^2 = \begin{pmatrix}-\sigma_i^2 & 0\\ 0 & -\sigma_i^2\end{pmatrix} = \begin{pmatrix}-\mathbb{1} & 0\\ 0 & -\mathbb{1}\end{pmatrix} = -\mathbb{1} \tag{99}$$

And the other conditions are of course:

$$\gamma_0\gamma_i + \gamma_i\gamma_0 = \begin{pmatrix}1 & 0\\ 0 & -1\end{pmatrix}\begin{pmatrix}0 & -\sigma_i\\ \sigma_i & 0\end{pmatrix} + \begin{pmatrix}0 & -\sigma_i\\ \sigma_i & 0\end{pmatrix}\begin{pmatrix}1 & 0\\ 0 & -1\end{pmatrix} = 0 \tag{100}$$

$$\begin{aligned}\gamma_i\gamma_j + \gamma_j\gamma_i &= \begin{pmatrix}0 & -\sigma_i\\ \sigma_i & 0\end{pmatrix}\begin{pmatrix}0 & -\sigma_j\\ \sigma_j & 0\end{pmatrix} + \begin{pmatrix}0 & -\sigma_j\\ \sigma_j & 0\end{pmatrix}\begin{pmatrix}0 & -\sigma_i\\ \sigma_i & 0\end{pmatrix}\\ &= \begin{pmatrix}-\sigma_i\sigma_j & 0\\ 0 & -\sigma_i\sigma_j\end{pmatrix} + \begin{pmatrix}-\sigma_j\sigma_i & 0\\ 0 & -\sigma_j\sigma_i\end{pmatrix} = 0 \text{ if } i \neq j \text{ (because } \sigma_i^2 = \mathbb{1})\end{aligned} \tag{101}$$

The total matrix equation for 3 dimensions of space and 1 of time is thus:

$$\begin{aligned}(\not{p} - mc^2)\Psi &= \begin{pmatrix}\mathbb{1}i\hbar\frac{\partial}{\partial t} - mc^2\mathbb{1} & i\hbar c\sum_{i=1}^{3}(\sigma_i\frac{\partial}{\partial x_i})\\ -i\hbar c\sum_{i=1}^{3}(\sigma_i\frac{\partial}{\partial x_i}) & -\mathbb{1}i\hbar\frac{\partial}{\partial t} - mc^2\mathbb{1}\end{pmatrix}\Psi = 0\\ &\text{where } \Psi = \begin{pmatrix}\psi_1(x_1,x_2,x_3,t)\\ \psi_2(x_1,x_2,x_3,t)\\ \psi_3(x_1,x_2,x_3,t)\\ \psi_4(x_1,x_2,x_3,t)\end{pmatrix}\end{aligned} \tag{102}$$

*Note: when looking for this $\not{p}$ relativistic energy operator, we have been ignoring the fact that the original energy equation is squared such that there would be a positive and negative solutions:

$$\not{p}^2 = E^2 - p^2c^2 = m^2c^4 \implies \not{p} = mc^2, \cancel{-mc^2} \tag{103}$$

However, this negative solution is not physically sensible and doesn't lead to any new physics.

Furthermore, what Dirac found out is that actually he was not just describing a particle by itself, but one in a vacuum that isn't empty and that this vacuum can have energy. But, we will not go into this. Instead we will focus on Dirac wave mechanics with no potential.

With this in mind, our next goal in solving this is to find an operator that is hermitian. $\not{p}$ is not hermitian as shown below:

$$\sigma_i^\dagger = \sigma_i \tag{104}$$

$$\gamma_0^\dagger = \gamma_0 \tag{105}$$

$$\gamma_i^\dagger = -\gamma_i \tag{106}$$

$$\therefore \not{p}^\dagger = i\hbar\gamma_0 + i\hbar c(\gamma_1\frac{\partial}{\partial x} + \gamma_2\frac{\partial}{\partial y} + \gamma_3\frac{\partial}{\partial z}) \neq \not{p} \tag{107}$$

So, instead let's see what happens when we do $\gamma_0\not{p}\gamma_0$:

$$\begin{aligned}\gamma_0 \not{\partial} \gamma_0 &= i\hbar\gamma_0^3 \frac{\partial}{\partial t} - i\hbar c \left[\gamma_0\gamma_1\gamma_0 \frac{\partial}{\partial x} + \gamma_0\gamma_2\gamma_0 \frac{\partial}{\partial y} + \gamma_0\gamma_3\gamma_0 \frac{\partial}{\partial z}\right] \\ &= i\hbar\gamma_0 \frac{\partial}{\partial t} - i\hbar c \left[-\gamma_1\gamma_0\gamma_0 \frac{\partial}{\partial x} - \gamma_2\gamma_0\gamma_0 \frac{\partial}{\partial y} - \gamma_3\gamma_0\gamma_0 \frac{\partial}{\partial z}\right] \\ &= i\hbar\gamma_0 \frac{\partial}{\partial t} + i\hbar c \left[\gamma_1 \frac{\partial}{\partial x} + \gamma_2 \frac{\partial}{\partial y} + \gamma_3 \frac{\partial}{\partial z}\right] = \not{\partial}^\dagger\end{aligned} \tag{108}$$

We can rearrange this to find a new operator that <u>is</u> hermitian:

$$\gamma_0 \not{\partial} \gamma_0 = \not{\partial}^\dagger \implies \not{\partial}\gamma_0 = \gamma_0 \not{\partial}^\dagger = (\not{\partial}\gamma_0)^\dagger \tag{109}$$

Alternatively we can use this operator:

$$\gamma_0 \not{\partial} = \not{\partial}^\dagger \gamma_0 = (\gamma_0 \not{\partial})^\dagger \tag{110}$$

*Note, remembering (98), we see that instead of these solutions of γ_i, there are also solutions of$-\gamma_i$.

Anyways, now we can write $\gamma_0(\not{\partial} - mc^2)\Psi(x, y, z, t) = 0$, which will look like this:

$$\begin{pmatrix} \mathbb{1} & 0 \\ 0 & -\mathbb{1} \end{pmatrix} \begin{pmatrix} \mathbb{1} i\hbar \frac{\partial}{\partial t} - mc^2\mathbb{1} & i\hbar c \sum_{i=1}^3 (\sigma_i \frac{\partial}{\partial x_i}) \\ -i\hbar c \sum_{i=1}^3 (\sigma_i \frac{\partial}{\partial x_i}) & -\mathbb{1} i\hbar \frac{\partial}{\partial t} - mc^2\mathbb{1} \end{pmatrix} \Psi = 0$$
$$\text{where } \Psi = \begin{pmatrix} \psi_1(x_1, x_2, x_3, t) \\ \psi_2(x_1, x_2, x_3, t) \\ \psi_3(x_1, x_2, x_3, t) \\ \psi_4(x_1, x_2, x_3, t) \end{pmatrix} \tag{111}$$

We can also rewrite Ψ into two 2-component vectors to match the notation style of the rest of the equation. Also, writing out the sums explicitly. This results in:

$$\begin{pmatrix} \mathbb{1} i\hbar \frac{\partial}{\partial t} - mc^2\mathbb{1} & i\hbar c(\sigma_1 \frac{\partial}{\partial x} + \sigma_2 \frac{\partial}{\partial y} + \sigma_3 \frac{\partial}{\partial z}) \\ i\hbar c(\sigma_1 \frac{\partial}{\partial x} + \sigma_2 \frac{\partial}{\partial y} + \sigma_3 \frac{\partial}{\partial z}) & \mathbb{1} i\hbar \frac{\partial}{\partial t} + mc^2\mathbb{1} \end{pmatrix} \begin{pmatrix} \psi_L(x, y, z, t) \\ \psi_R(x, y, z, t) \end{pmatrix} = 0 \tag{112}$$

So, let's write the matrix equations this correlates to more explicitly:

$$i\hbar \frac{\partial \psi_L}{\partial t} - mc^2\psi_L + i\hbar c \left[\sigma_1 \frac{\partial}{\partial x} + \sigma_2 \frac{\partial}{\partial y} + \sigma_3 \frac{\partial}{\partial z}\right] \psi_R = 0 \tag{113}$$

$$i\hbar c \left[\sigma_1 \frac{\partial}{\partial x} + \sigma_2 \frac{\partial}{\partial y} + \sigma_3 \frac{\partial}{\partial z}\right] \psi_L + i\hbar \frac{\partial \psi_L}{\partial t} + mc^2\psi_R = 0 \tag{114}$$

$$\psi_L(x, y, z, t) = \chi_L e^{\frac{i}{\hbar}(p_1 x + p_2 y + p_3 z - Et)} \tag{115}$$

$$\psi_R(x, y, z, t) = \chi_R e^{\frac{i}{\hbar}(p_1 x + p_2 y + p_3 z - Et)} \tag{116}$$

Equation (113) can thus be written as:

$$\{E\chi_L - mc^2\chi_L - c[\sigma_1 p_1 + \sigma_2 p_2 + \sigma_3 p_3]\chi_R\} e^{\frac{i}{\hbar}(p_1 x + p_2 y + p_3 z - Et)} = 0 \tag{117}$$

$$\implies (E - mc^2)\chi_L = c(\sigma_1 p_1 + \sigma_2 p_2 + \sigma_3 p_3)\chi_R \tag{118}$$

And (114):

$$\{-c[\sigma_1 p_1 + \sigma_2 p_2 + \sigma_3 p_3]\chi_L + E\chi_R + mc^2\chi_R\} e^{\frac{i}{\hbar}(p_1 x + p_2 y + p_3 z - Et)} = 0 \tag{119}$$

$$\implies (E + mc^2)\chi_R = c(\sigma_1 p_1 + \sigma_2 p_2 + \sigma_3 p_3)\chi_L \tag{120}$$

If we multiply (118) or (120) by $= c(\sigma_1 p_1 + \sigma_2 p_2 + \sigma_3 p_3)$ we end up with:

$$(E - mc^2)(E + mc^2)\chi_R = c^2(\sigma_1 p_1 + \sigma_2 p_2 + \sigma_3 p_3)^2\chi_R = c^2 p^2 \chi_R \tag{121}$$

$$(E + mc^2)(E - mc^2)\chi_L = c^2(\sigma_1 p_1 + \sigma_2 p_2 + \sigma_3 p_3)^2\chi_L = c^2 p^2 \chi_L \tag{122}$$

But let's not forget that χ_R and χ_L are both 2-component vectors, so we should write these as:

$$\begin{pmatrix} E^2 - m^2c^4 - p^2c^2 & 0 \\ 0 & E^2 - m^2c^4 - p^2c^2 \end{pmatrix} \begin{pmatrix} \chi_{R1} \\ \chi_{R2} \end{pmatrix} = 0 \tag{123}$$

$$\begin{pmatrix} E^2 - m^2c^4 - p^2c^2 & 0 \\ 0 & E^2 - m^2c^4 - p^2c^2 \end{pmatrix} \begin{pmatrix} \chi_{L1} \\ \chi_{L2} \end{pmatrix} = 0 \tag{124}$$

Since we know that $E^2 = p^2c^2 + m^2c^4$, the eigenvector solutions to (123) are:

$$\chi_R = \begin{pmatrix} 1 \\ 0 \end{pmatrix}, \begin{pmatrix} 0 \\ 1 \end{pmatrix} \tag{125}$$

And we can find the correspond χ_L vectors corresponding to these by rearranging (118):

$$\chi_L = \frac{c(\sum_{i=1}^{3} p_i \sigma_i)}{E - mc^2}\chi_R \tag{126}$$

Similarly, there will be a set of solutions:

$$\chi_L = \begin{pmatrix} 1 \\ 0 \end{pmatrix}, \begin{pmatrix} 0 \\ 1 \end{pmatrix} \tag{127}$$

Where the corresponding χ_R vectors would be found by rearranging (120):

$$\chi_R = \frac{c(\sum_{i=1}^{3} p_i \sigma_i)}{E + mc^2}\chi_L \tag{128}$$

This first solution set ((125) and (126)) we say is for $E < 0$ and the second is for $E > 0$ ((127) and (128)). We say that $E = 0$ is unphysical because it would be a massless particle at rest and how would you even detect that?

As we know, the total energy equation is $E^2 = m^2c^4 + p^2c^2$, meaning the energy could be:

$$|E| = \sqrt{m^2c^4 + p^2c^2} \tag{129}$$

$$E = \begin{cases} +\sqrt{m^2c^4 + p^2c^2} & \text{physical} \\ -\sqrt{m^2c^4 + p^2c^2} & \text{"unphysical"} \end{cases} \tag{130}$$

4.5 Solution of j=1/2

So, let's figure these out completely.

We know that:

$$c\left(\sum_{i=1}^{3} p_i\sigma_i\right) = \begin{pmatrix} -cp_3 & cp_1 + icp_2 \\ cp_1 - icp_2 & cp_3 \end{pmatrix} \tag{131}$$

If $\chi_R = \begin{pmatrix} 1 \\ 0 \end{pmatrix}, \begin{pmatrix} 0 \\ 1 \end{pmatrix}$ then finding the rest of the solution set (χ_L vectors involves plugging χ_R vectors into (121).

Similarly, if $\chi_L = \begin{pmatrix} 1 \\ 0 \end{pmatrix}, \begin{pmatrix} 0 \\ 1 \end{pmatrix}$ then finding the rest of the solution set (χ_R vectors involves plugging χ_R vectors into (123).

Placing both of these solution sets in a table:

	$E > 0$		$E < 0$	
	Solution 1	Solution 2	Solution 1	Solution 2
χ_L	1	0	$\frac{-cp_3}{-\lvert E\rvert - mc^2}$	$\frac{cp_1+icp_2}{-\lvert E\rvert - mc^2}$
	0	1	$\frac{cp_1-icp_2}{-\lvert E\rvert - mc^2}$	$\frac{cp_3}{-\lvert E\rvert - mc^2}$
χ_R	$\frac{-cp_3}{\lvert E\rvert + mc^2}$	$\frac{cp_1+icp_2}{\lvert E\rvert + mc^2}$	1	0
	$\frac{cp_1-icp_2}{\lvert E\rvert + mc^2}$	$\frac{cp_3}{\lvert E\rvert + mc^2}$	0	1

4.6 Orthogonality

Let's now examine the orthogonality between these vectors, starting with E¿0 Solutions 1 and 2:

$$\begin{pmatrix} 1 \\ 0 \\ \frac{-cp_3}{|E|+mc^2} \\ \frac{cp_1-icp_2}{|E|+mc^2} \end{pmatrix} \cdot \begin{pmatrix} 1 \\ 0 \\ \frac{-cp_3}{|E|+mc^2} \\ \frac{cp_1-icp_2}{|E|+mc^2} \end{pmatrix} \tag{132}$$

$$= 0 + 0 + \left(\frac{-cp_3}{E+mc^2}\right)\left(\frac{cp_1+icp_2}{E+mc^2}\right) + \left(\frac{cp_1+icp_2}{E+mc^2}\right)\left(\frac{cp_3}{E+mc^2}\right) = 0$$

Likewise we find that between $E > 0$ and $E < 0$ solutions there is also orthogonality. Between $E > 0$ Solution 1 and $E < 0$ Solution 1:

$$\begin{pmatrix} 1 \\ 0 \\ \frac{-cp_3}{|E|+mc^2} \\ \frac{cp_1-icp_2}{|E|+mc^2} \end{pmatrix} \cdot \begin{pmatrix} \frac{-cp_3}{-|E|-mc^2} \\ \frac{cp_1-icp_2}{-|E|-mc^2} \\ 1 \\ 0 \end{pmatrix} = \frac{-cp_3}{-|E|-mc^2} - \frac{-cp_3}{|E|+mc^2} = 0 \tag{133}$$

And here is another example for $E > 0$ Solution 1 and $E < 0$ Solution 2 (remembering that since this is an inner product we take the complex conjugate of the first vector):

$$\begin{pmatrix} 1 \\ 0 \\ \frac{-cp_3}{|E|+mc^2} \\ \frac{cp_1-icp_2}{|E|+mc^2} \end{pmatrix} \cdot \begin{pmatrix} \frac{cp_1+icp_2}{-|E|-mc^2} \\ \frac{cp_3}{-|E|-mc^2} \\ 1 \\ 0 \end{pmatrix} = \frac{cp_1+icp_2}{-|E|-mc^2} + \frac{cp_1+icp_2}{|E|+mc^2} = 0 \tag{134}$$

In summary:

$$\begin{aligned} \psi_{+1}^\dagger \psi_{+2} &= 0 \\ \psi_{+1}^\dagger \psi_{-1} &= 0 \\ \psi_{+2}^\dagger \psi_{-1} &= 0 \\ \psi_{+1}^\dagger \psi_{-2} &= 0 \\ \psi_{+2}^\dagger \psi_{-2} &= 0 \\ \psi_{-1}^\dagger \psi_{-2} &= 0 \end{aligned} \tag{135}$$

4.7 Normalization

However, these wave function vectors are not yet normalized. In order to normalize we find the "length".

For example, the "length^2" (inner product with itself) of Solution 1 of $E > 0$ is:

$$\begin{aligned} &1 + \frac{c^2p_3^2}{(|E|+mc^2)^2} + \frac{c^2p + 1^2 + c^2p_2^2}{(|E|+mc^2)^2} = 1 + \frac{c^2p^2}{(|E|+mc^2)^2} \\ &= 1 + \frac{|E|^2 - m^2c^4}{(|E|+mc^2)^2} = 1 + \frac{\cancel{(|E|+mc^2)}(|E|-mc^2)}{\cancel{(|E|+mc^2)}(|E|+mc^2)} = \frac{2|E|}{|E|+mc^2} \end{aligned} \tag{136}$$

The result is the same for the rest of the solutions, meaning the normalization constant we must multiply each solution term by is:

$$\frac{1}{\text{length}} = \sqrt{\frac{|E|+mc^2}{2|E|}} \tag{137}$$

So, the solutions when they are normalized look as follows:

	$E > 0$		$E < 0$	
	Solution 1	Solution 2	Solution 1	Solution 2
χ_L	$\sqrt{\frac{\lvert E\rvert+mc^2}{2\lvert E\rvert}}$	0	$\sqrt{\frac{\lvert E\rvert+mc^2}{2\lvert E\rvert}}\frac{-cp_3}{-\lvert E\rvert-mc^2}$	$\sqrt{\frac{\lvert E\rvert+mc^2}{2\lvert E\rvert}}\frac{cp_1+icp_2}{-\lvert E\rvert-mc^2}$
	0	$\sqrt{\frac{\lvert E\rvert+mc^2}{2\lvert E\rvert}}$	$\sqrt{\frac{\lvert E\rvert+mc^2}{2\lvert E\rvert}}\frac{cp_1-icp_2}{-\lvert E\rvert-mc^2}$	$\sqrt{\frac{\lvert E\rvert+mc^2}{2\lvert E\rvert}}\frac{cp_3}{-\lvert E\rvert-mc^2}$
χ_R	$\sqrt{\frac{\lvert E\rvert+mc^2}{2\lvert E\rvert}}\frac{-cp_3}{\lvert E\rvert+mc^2}$	$\sqrt{\frac{\lvert E\rvert+mc^2}{2\lvert E\rvert}}\frac{cp_1+icp_2}{\lvert E\rvert+mc^2}$	$\sqrt{\frac{\lvert E\rvert+mc^2}{2\lvert E\rvert}}$	0
	$\sqrt{\frac{\lvert E\rvert+mc^2}{2\lvert E\rvert}}\frac{cp_1-icp_2}{\lvert E\rvert+mc^2}$	$\sqrt{\frac{\lvert E\rvert+mc^2}{2\lvert E\rvert}}\frac{cp_3}{\lvert E\rvert+mc^2}$	0	$\sqrt{\frac{\lvert E\rvert+mc^2}{2\lvert E\rvert}}$

Between the two solutions for $E > 0$ we know that Solution 1 can be interpreted as the negative spin state and Solution 2 can be interpreted as the positive spin state because:

$$\sigma_3 \begin{pmatrix} 1 \\ 0 \end{pmatrix} = -1 \begin{pmatrix} 1 \\ 0 \end{pmatrix} \tag{138}$$

Meaning $m_z = \frac{-1}{2}$. Likewise:

$$\sigma_3 \begin{pmatrix} 0 \\ 1 \end{pmatrix} = 1 \begin{pmatrix} 0 \\ 1 \end{pmatrix} \tag{139}$$

The same is true for $E < 0$ where Solution 1 is $m_z = \frac{-1}{2}$ and Solution 2 is $m_z = \frac{1}{2}$

Let's now think about what happens with a particle at rest. For a particle at rest with a certain mass, we know that $p_i = 0$ and $E = mc^2$. Therefore our solutions for $E > 0$ become:

$$\text{Solution 1} = \begin{pmatrix} 1 \\ 0 \\ 0 \\ 0 \end{pmatrix} \tag{140}$$

$$\text{Solution 2} = \begin{pmatrix} 0 \\ 1 \\ 0 \\ 0 \end{pmatrix} \tag{141}$$

This makes the above claim about the spin state of each solution even more clear.

4.8 Charge

It turns out, $\psi^\dagger \gamma_0 \psi$ has a physical meaning that can be understood as telling you about the charge (or the direction in time). We don't need to integrate this value over x or t because they cancel out. Furthermore, overall we find that:

$$\psi^\dagger \gamma_\mu \psi = (\rho, \vec{j}) \tag{142}$$

Where ρ is the charge density and $\vec{j}$ is the current density which together make the four-current.

Let's apply this to the case of a particle at rest ($\vec{\rho} = 0$). The solutions to this are:

$$E > 0\text{: and } E < 0\text{:}$$

$$\begin{pmatrix}1\\0\\0\\0\end{pmatrix}, \begin{pmatrix}0\\1\\0\\0\end{pmatrix} \quad \begin{pmatrix}0\\0\\1\\0\end{pmatrix}, \begin{pmatrix}0\\0\\0\\1\end{pmatrix} \tag{143}$$

Performing $\psi^\dagger \gamma_0 \psi$ (γ_0 defined in (93) on each of these respectively yields:

$$+1,\ +1,\ -1,\ -1$$

Since we want to interpret this as physical charge, we don't want this quantity to change with momentum so for the case of the first solution in (143):

$$\psi^\dagger_{+1}\gamma_0\psi_{+1} = 1 - \frac{c^2p_3^2}{(|E|+mc^2)^2} - \frac{c^2(p_1^2+p_2^2)}{(|E|+mc^2)^2} = 1 - \frac{c^2p^2}{(|E|+mc^2)^2} = 1 - \frac{|E|-mc^2}{|E|+mc^2} = \frac{2mc^2}{|E|+mc^2} \tag{144}$$

So, unlike before where we just used $\psi^\dagger\psi$ we use $\psi^\dagger\gamma_0\psi$ to normalize.

In that case our normalization constant would be $\sqrt{\frac{|E|+mc^2}{2mc^2}}$.

So our normalized solution set <u>for a particle at rest</u> becomes:

$$\begin{pmatrix}\sqrt{\frac{|E|+mc^2}{2mc^2}}\\0\\0\\0\end{pmatrix}, \begin{pmatrix}0\\\sqrt{\frac{|E|+mc^2}{2mc^2}}\\0\\0\end{pmatrix} \quad \begin{pmatrix}0\\0\\\sqrt{\frac{|E|+mc^2}{2mc^2}}\\0\end{pmatrix}, \begin{pmatrix}0\\0\\0\\\sqrt{\frac{|E|+mc^2}{2mc^2}}\end{pmatrix}$$

But we want to extend this outside of just particle at rest solutions. So we will find some matrix of these γ_0 to normalize and find orthogonality that has components:

$$\psi_i \gamma_0 \psi_j \tag{145}$$

This matrix looks like this:

$$\psi_i\gamma_0\psi_j = \begin{pmatrix} \psi_{+1}\gamma_0\psi_{+1} & \psi_{+2}\gamma_0\psi_{+1} & \psi_{-1}\gamma_0\psi_{+1} & \psi_{-2}\gamma_0\psi_{+1} \\ \psi_{+1}\gamma_0\psi_{+2} & \psi_{+2}\gamma_0\psi_{+2} & \psi_{-1}\gamma_0\psi_{+2} & \psi_{-2}\gamma_0\psi_{+2} \\ \psi_{+1}\gamma_0\psi_{-1} & \psi_{+2}\gamma_0\psi_{-1} & \psi_{-1}\gamma_0\psi_{-1} & \psi_{-2}\gamma_0\psi_{-1} \\ \psi_{+1}\gamma_0\psi_{-2} & \psi_{+2}\gamma_0\psi_{-2} & \psi_{-1}\gamma_0\psi_{-2} & \psi_{-2}\gamma_0\psi_{-2} \end{pmatrix} = \begin{pmatrix} 1 & 0 & \frac{p_3}{mc} & \frac{-p_1-ip_2}{mc} \\ 0 & 1 & \frac{-p_1+ip_2}{mc} & \frac{-p_3}{mc} \\ \frac{p_3}{mc} & \frac{-p_1+ip_2}{mc} & -1 & 0 \\ \frac{-p_1-ip_2}{mc} & \frac{-p_3}{mc} & 0 & -1 \end{pmatrix} \tag{146}$$

As you can tell, the terms that are crossed between negative and positive charge values are non-zero, meaning they are not orthogonal with each other in this way. The implications of this are to be expanded on.

4.9 Adding a magnetic field

Let's define a magnetic field in the z direction:

$$\vec{B} = B\hat{z},\ \ e(>0) \tag{147}$$

$$\vec{F} = e\vec{V} \times \vec{B} \tag{148}$$

$$\implies \frac{d\vec{V}}{dt} = \frac{eB}{m}\vec{V} \times \hat{z} = \frac{eB}{m}(v_x\hat{x} + v_y\hat{y} + v_z\hat{z}) \times \hat{z} = -v_x\hat{y} + v_y\hat{x} \tag{149}$$

$$\frac{dv_x}{dt} = \frac{eB}{m}v_y \tag{150}$$

$$\frac{dv_y}{dt} = \frac{eB}{m}v_x \tag{151}$$

$$\frac{dv_z}{dt} = 0 \tag{152}$$

$$v_x = v_0 sin(\frac{eB}{m}t) \tag{153}$$

$$v_y = v_0 cos(\frac{eB}{m}t) \tag{154}$$

where $\frac{eB}{m}$ is the cyclotron frequency and $v_0 = v_x^2 + v_y^2$

$$\vec{v} = v_0[sin(\omega t)\hat{x} + cos(\omega t)\hat{y}] \tag{155}$$

$$\vec{r} = \frac{v_0}{\omega}[-cos(\omega t)\hat{x} + sin(\omega t)\hat{y}] \tag{156}$$

$$\vec{L} = m\vec{r} \times \vec{v} = \frac{mv_0^2}{\omega}[\hat{z}] = \frac{mv_0^2}{\frac{eB}{m}}\hat{z} = \frac{m^2v_0^2}{eB}\hat{z} = e\frac{m^2v_0^2}{e^2B^2}B\hat{z} = \frac{ev_0^2}{\omega^2}B\hat{z} \tag{157}$$

where $\frac{ev_0^2}{\omega^2}$ is a property of the charged particle.

$$\vec{L} \cdot \vec{B} = \frac{mv_0^2 B}{\omega} = \frac{m^2 v_0^2 \cancel{B}}{e\cancel{B}} = \frac{m^2 v_0^2}{e} \tag{158}$$

Total energy is thus the sum of the free kinetic energy, the potential energy, and the kinetic energy due to the magnetic field:

$$\text{Total Energy} = \frac{p^2}{2m} + V(r) + \frac{1}{2}\frac{e}{m}\vec{L} \cdot \vec{B} \tag{159}$$

Let's just note that $\frac{e}{m}$ is a property of the particle, $\vec{L}$ is a property of the motion, and $\vec{B}$ is the external applied field.

We will define $\mu = \frac{e}{2m}$.

So now we will look at a new hamiltonian that we will define as $H_B = H + \mu\vec{L} \cdot \vec{B}$. Our new wave equation becomes:

$$\left\{ \frac{-\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right) + V(r) + \mu\vec{L} \cdot \vec{B} \right\} \psi(x,y,z,t) = i\hbar\frac{\partial}{\partial t}\psi(x,y,z,t) \tag{160}$$

$$\left\{ \frac{-\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right) + V(r) + \mu\vec{L} \cdot \vec{B} \right\} \psi(x,y,z) = E\psi(x,y,z) \tag{161}$$

Let's compare how this affects our energy level solutions by summarizing. Before we had picked a set of operators that commute:

$$\begin{gathered} [H, L^2] = 0 \\ [H, L_a] = 0 \\ [L^2, L_a] \end{gathered} \tag{162}$$

where $a = 1, 2, 3$

With this we ended up with:

$$[L_a, L_b] = i\hbar\mathcal{E}_{abc}L_c \tag{163}$$

With this we were able to obtain a wave function $\psi_{n,j,m}(r,\theta,\phi) = |n,j,m\rangle$ and perform the operators on it:

$$L_z |n,j,m\rangle = \hbar m |n,j,m\rangle \tag{164}$$

$$L^2 |n,j,m\rangle = \hbar^2 j(J+1) |n,j,m\rangle \tag{165}$$

$$H |n,j,m\rangle = E_n |n,j,m\rangle = \left(-\frac{1}{2}\left[\frac{Ze^2}{4\pi\mathcal{E}_0}\right]^2 \frac{m_e}{\hbar^2}\frac{1}{n^2} \right) |n,j,m\rangle \tag{166}$$

Now, with the introduction of a magnetic field we have our new operator $H_B = H + \mu\vec{L} \cdot \vec{B}$. The operation thus becomes (if $\vec{L} = L_z\hat{z}$:

$$H\left|n,j,m\right\rangle = H\left|n,j,m\right\rangle + \mu\vec{L}\cdot\vec{B}\left|n,j,m\right\rangle = E_n\left|n,j,m\right\rangle + \frac{eB}{2m_e}L_z\left|n,j,m\right\rangle$$
$$= E_n\left|n,j,m\right\rangle + \frac{eB}{2m_e}\hbar m\left|n,j,m\right\rangle \tag{167}$$

The direction of the magnetic field should not matter, so we should end up with the same result for $\vec{B} = B\hat{x}$ where $\vec{L}\cdot\vec{B} = L_x B$

$$\frac{1}{8\pi b^3}e^{-\frac{r}{b}}r^3 sin\theta \tag{168}$$

(169)

Quantum Mechanics- Part 7, Perturbation Theory

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Contents

1 Perturbation Theory

1.1 Motivation

We defined the Hamiltonian:

$$H\psi(x,y,z,t) = i\hbar\frac{\partial}{\partial t}\psi(x,y,z,t) \tag{1}$$

Based on wave functions of this type we find that this Hamiltonian extracts the energy of the wave in a stationary state:

$$\psi = \phi(x,y,z)e^{\frac{-iE}{\hbar}t} \tag{2}$$

$$H\phi = E\phi \tag{3}$$

We can define the entire wave function based on separate functions of the following type which we have previously defined in more detail:

$$|n=1, j=1, m=-1\rangle = \left[R_n^J(r)P_j^m(\theta)e^{im\phi}\right]e^{\frac{-iE}{\hbar}t} \tag{4}$$

The question becomes, with this setup, how do we go from this state to one of a higher value of j? The reality is that we have assumed that the state is the same one over time. In more advanced quantum mechanics courses, perturbation theory is used to show time dependent changes in state.

Side note: H_2 Experiment

In the hydrogen gas experiment, there is a current run through hydrogen gas and the current is controlled by a switch

There is a $\delta V(r,t)$ that happens whenever the switch is opened or closed (gas is deexcited or excited). Perturbation theory shows one method for dealing with these changes in the potential energy.

1.2 Perturbed Hamiltonian and Wave Functions

We know that H_0 (with no perturbation) can be solved exactly:

$$H_0\,|n\rangle = E_n\,|n\rangle \tag{5}$$

(By the way, these $|n\rangle$'s are not necessarily referring to the n quantum number from the hydrogenic atoms solution.)

However, H (including a perturbation) cannot be solved exactly, where H is:

$$H = H_0 + \lambda V_1(r)\ \lambda \text{ is "small"} \tag{6}$$

We will denote this complete hamiltonian and solution set as:

$$H\,|\phi\rangle = E_\phi\,|\phi\rangle \tag{7}$$

$$(H_0 + \lambda V_1)\,|\phi\rangle = E_\phi\,|\phi\rangle \tag{8}$$

However, we can rewrite these energies and solution sets as:

$$|\phi\rangle = \sum_{k=0}^{\infty} \lambda^k\,|\phi_k\rangle \text{ and } E_\phi = \sum_{k=0}^{\infty} \lambda^k \mu_k \tag{9}$$

With this we can rewrite (12) as:

$$\begin{aligned}&(H_0 + \lambda V_1)(|\phi_0\rangle + \lambda\,|\phi_1\rangle + \lambda^2\,|\phi_2\rangle + ...)\\ &= (\mu_0 + \lambda\mu_1 + \lambda^2\mu_2 + ...)(|\phi_0\rangle + \lambda\,|\phi_1\rangle + \lambda^2\,|\phi_2\rangle + ...)\end{aligned} \tag{10}$$

Since λ can be anything, equation (14) must be true for each term of λ. So for λ to the power of 0:

$$\underline{\lambda^0}$$

$$H_0\,|\phi_0\rangle = \mu_0\,|\phi_0\rangle \tag{11}$$

We see that these $|\phi_0\rangle$ are just the unperturbed solutions of H_0, where:

$$|\phi_0\rangle = |n\rangle \text{ and } \mu_0 = E_n \tag{12}$$

Then for λ to first power:

$$\underline{\lambda^1}$$

$$\begin{aligned}&H_0\,|\phi_1\rangle + V_1\,|\phi_0\rangle = \mu_0\,|\phi_1\rangle + \mu_1\,|\phi_0\rangle\\ \implies &(H_0 - \mu_0)\,|\phi_1\rangle = \mu_1\,|\phi_0\rangle - V_1\,|\phi_0\rangle\\ &= \mu_1\,|\phi_0\rangle - V_1\,|n\rangle\end{aligned} \tag{13}$$

To this equation we can apply $\langle n|$:

$$\langle n|(H_0 - E_n)|\phi_1\rangle = \mu_1\,\langle n|n\rangle - \langle n|V_1|n\rangle \tag{14}$$

Since we know that $\langle n|\,H_0 = E_n\,\langle n|$. This can be rewritten as:

$$\begin{aligned}E_n\,\langle n|\phi_1\rangle - E_n\,\langle n|\phi_1\rangle = 0 &= \mu_1 - \langle n|V_1|n\rangle\\ \implies \mu_1 &= \langle n|V_1|n\rangle\end{aligned} \tag{15}$$

These are the energy solutions for μ_1 which we can use to find a closer value to the total perturbed energy. Now let's find the actual states (eigenvectors) of this order λ^1. First, we think about how how any vector can be rewritten as a linear combination of eigenvectors of H_0:

$$|\phi_1\rangle = \sum C_{1m}\,|m\rangle \tag{16}$$

Where these constants C_{1m} are complex numbers.
So (17) is rewritten as:

$$
\begin{aligned}
&(H_0 - E_n)(\sum C_{1m} |m\rangle) = \mu_1 |n\rangle - V_1 |n\rangle \\
\implies &\sum C_{1m}(H_0 - E_n) |m\rangle = \mu_1 |n\rangle - V_1 |n\rangle \\
\implies &\sum C_{1m}(E_m - E_n) |m\rangle = \mu_1 |n\rangle - V_1 |n\rangle
\end{aligned} \tag{17}
$$

Then we take inner product with $\langle k|$:

$$
\begin{aligned}
\sum C_{1m}(E_m - E_n) \langle k|m\rangle &= \mu_1 \langle k|n\rangle - \langle k|V_1|n\rangle \\
\implies C_{1k}(E_k - E_n) &= \mu_1 \delta_{kn} - \langle k|V_1|n\rangle \\
\implies C_{1k} &= \frac{\mu_1 \delta_{kn} - \langle k|V_1|n\rangle}{E_k - E_n}
\end{aligned} \tag{18}
$$

If $k \neq n$ then:

$$
C_{1k} = \frac{-\langle k|V_1|n\rangle}{E_k - E_n} \tag{19}
$$

With this we can finally write our vectors $|\phi_1\rangle$ in terms of this constant:

$$
|\phi_1\rangle = \sum_m C_{1m} |m\rangle = C_{1n} |n\rangle + \sum_{m \neq n} \frac{\langle m|V_1|n\rangle}{E_n - E_m} |m\rangle \tag{20}
$$

So we're closer to knowing the perturbed states and their energies:

$$
|\phi\rangle = |\phi_0\rangle + \lambda |\phi_1\rangle + ... = (1 + \lambda C_{1n}) |n\rangle + \lambda \sum_{m \neq n} \frac{\langle m|V_1|n\rangle}{E_n - E_m} + ... \tag{21}
$$

where C_{1n} is fixed by normalization. The energies:

$$
E_\phi = \mu_0 + \lambda \mu_1 + ... = E_n + \lambda \langle n|V_1|n\rangle + ... \tag{22}
$$

The λ to the second order:

$$
\underline{\lambda^2}
$$

$$
\begin{aligned}
&H_0 |\phi_2\rangle + V_1 |\phi_1\rangle = \mu_0 |\phi_2\rangle + \mu_1 |\phi_1\rangle + \mu_2 |\phi_0\rangle \\
\implies &(H_0 - \mu_0) |\phi_2\rangle = \mu_2 |\phi_0\rangle + \mu_1 |\phi_1\rangle - V_1 |\phi_1\rangle
\end{aligned} \tag{23}
$$

For this order of λ we use the same trick as for λ^1, rewriting the states as a sum of other states:

$$
|\phi_2\rangle = \sum C_{2k} |k\rangle \tag{24}
$$

For clarity we will now also refer to $|\phi_1\rangle$ as the sum $|\phi_1\rangle = \sum C_{1l} |l\rangle$
So, equation (27) becomes:

$$
\sum_k C_{2k}(H_0 - E_n) |k\rangle = \sum_l C_{1l}(\mu_1 - V_1) |l\rangle + \mu_2 |n\rangle \tag{25}
$$

Now we take the inner product with $\langle m|$:

$$\sum_k C_{2k}(E_k - E_n)\delta_{km} = \sum_l C_{1l}(\mu_1 \delta_{ml} - \langle m|V_1|l\rangle) + \mu_2 \delta_{mn} \tag{26}$$

If $m = n$:

$$\begin{aligned} 0 &= \mu_1 C_{1n} - \sum_l C_{1l} \langle n|V_1|l\rangle + \mu_2 \\ &= \mu_1 C_{1n} - C_{1n} \langle n|V_1|n\rangle - \sum_{l\neq n} \langle n|V_1|l\rangle + \mu_2 \\ &= \mu_1 C_{1n} - \mu_1 C_{1n} - \sum_{l\neq n} \langle n|V_1|l\rangle + \mu_2 \\ \implies \mu_2 &= \sum_{l\neq n} C_{1l} \langle n|V_1|l\rangle = \sum_{l\neq n} \frac{\langle l|V_1|n\rangle \langle n|V_1|l\rangle}{E_n - E_l} \end{aligned} \tag{27}$$

If $m \neq n$:

$$C_{2m} = \frac{\mu_1 C_{1m} - \sum_l C_{1l} \langle m|V_1|l\rangle}{E_m - E_n} \tag{28}$$

Once more using these we end up with something closer to the perturbed state and energies:

$$|\phi_2\rangle = C_{2k}|k\rangle + \sum_{k\neq m} \left[\frac{\langle k|V'|m\rangle}{E_m - E_k} \left(1 - \frac{\langle m|V'|m\rangle}{E_m - E_k}\right) + \sum_{k\neq n} \frac{\langle k|V'|n\rangle \langle n|V'|m\rangle}{(E_m - E_k)(E_m - E_n)} \right] \tag{29}$$

$$\begin{aligned} E_\phi &= E_n + \langle n|V'|n\rangle + \sum_{l\neq n} \frac{|\langle l|V'|n\rangle|^2}{E_n - E_l} \\ &= E_n + \langle n|V'|n\rangle + \sum_{l\neq n} \frac{\langle n|V'|l\rangle \langle l|V'|n\rangle}{E_n - E_l} \end{aligned} \tag{30}$$

If we were to continue this pattern we could look for the third order of the perturbed states:

$$\underline{\lambda^3}$$

$$(H_0 - \mu_0)|\phi_3\rangle = \mu_3|\phi_0\rangle + \mu_2|\phi_1\rangle + \mu_1|\phi_2\rangle - V_1|\phi_2\rangle \tag{31}$$

1.3 Perturbation Theory with Degenerate States

It may happen that there are unperturbed degenerate states that are affected differently by an added potential or perturbation, making them non-degenerate.

More specifically had assumed that all for E_n all $m \neq n$ were such that $E_m - E_m \neq 0$ but this isn't necessarily true.

So, let's assume that $E_n = E_{n+1} = \mu_0$. This means that some unperturbed $|\phi_0\rangle$ can be any linear combination of the two of them:

$$|\phi_0\rangle = C_n |n\rangle + C_{n+1} |n+1\rangle \tag{32}$$

This $|\phi_0\rangle$ will have the same energy for any choice of C_n and C_{n+1} so it can be any linear combination of $|n\rangle$ and $|n+1\rangle$.

We will do the same trick of writing the next wave function as a sum of vectors:

$$|\phi_1\rangle = \sum_k C_{1k} |k\rangle \tag{33}$$

Plugging into the equation from the first order of lambda (13):

$$\begin{aligned} &(H_0 - E_n)(\sum_k C_{1k} |k\rangle) = (\mu_1 - V_1)(C_n |n\rangle + C_{n+1} |n+1\rangle) \\ \implies &\sum_k C_{1k}(E_k - E_n) |k\rangle = (\mu_1 - V_1)(C_n |n\rangle + C_{n+1} |n+1\rangle) \end{aligned} \tag{34}$$

Then we take the inner products with both $|n\rangle$ and $|n+1\rangle$:

$$\sum_k C_{1k}(E_k - E_n)\delta_{k,n} = \mu_1 C_n - C_n \langle n|V_1|n\rangle - C_{n+1} \langle n|V_1|n+1\rangle \tag{35}$$

$$\sum_k C_{1k}(E_k - E_n)\delta_{k,n+1} = \mu_1 C_{n+1} - C_n \langle n+1|V_1|n\rangle - C_{n+1} \langle n+1|V_1|n+1\rangle \tag{36}$$

Finally, we can write this system of equations as a matrix and solve for the values of μ_1:

$$\begin{pmatrix} \langle n|V_1|n\rangle & \langle n|V_1|n+1\rangle \\ \langle n+1|V_1|n\rangle & \langle n+1|V_1|n+1\rangle \end{pmatrix} \begin{pmatrix} C_n \\ C_{n+1} \end{pmatrix} = \mu_1 \begin{pmatrix} C_n \\ C_{n+1} \end{pmatrix} \tag{37}$$

We want to find both the eigenvalues and eigenvectors of this equation.

**Note, in order for our values of energy to make physical sense, we don't want them to be complex. Therefore, V_1 must be hermitian:

$$(\langle n|V_1|n+1\rangle)^* = \langle n+1|V_1|n\rangle \tag{38}$$

2 Examples of Perturbation Theory

2.1 1D Harmonic Oscillator with $V_1 = x$

We know that for our perturbed states, the new energy (to the second order) becomes:

$$E_\phi = E_n + \langle n|V_1|n\rangle + \sum_{l\neq n} \frac{\langle n|V_1|l\rangle \langle l|V_1|n\rangle}{E_n - E_l} \tag{39}$$

We also know that $x = \frac{\sqrt{2}b}{2}(a^\dagger + a)$. With this we can find the energy of a perturbation where $V_1 = x$:

$$\begin{aligned}
E_\phi &= E_n + \frac{\sqrt{2}b}{2}\langle n|a^\dagger + a|n\rangle + \frac{b^2}{2}\sum_{l\neq n}\frac{\langle n|a^\dagger + a|l\rangle \langle l|a^\dagger + a|n\rangle}{E_n - E_l} \\
&= E_n + \frac{\sqrt{2}b}{2}\left[\sqrt{n+1}\langle n|n+1\rangle + \sqrt{n}\langle n|n-1\rangle\right] \\
&+\frac{b^2}{2}\sum_{l\neq n}\frac{(\sqrt{l+1}\langle n|l+1\rangle + \sqrt{l}\langle n|l-1\rangle)(\sqrt{n+1}\langle l|n+1\rangle + \sqrt{n}\langle l|n-1\rangle)}{E_n - E_l} \\
&= E_n + \frac{b^2}{2}\sum_{l\neq n}\frac{(\sqrt{l+1}\delta_{n,l+1} + \sqrt{l}\delta_{n,l-1})(\sqrt{n+1}\delta_{l-1,n} + \sqrt{n}\delta_{l+1,n})}{E_n - E_l} \\
&= E_n + \frac{\sqrt{n}\sqrt{n}b^2}{2(E_n - E_{n-1})} + \frac{\sqrt{n+1}\sqrt{n+1}b^2}{2(E_n - E_{n+1})} \\
&= E_n + \frac{n(\frac{\hbar}{m\omega})}{2\hbar\omega} - \frac{(n+1)(\frac{\hbar}{m\omega})}{2\hbar\omega} \\
&= E_n + \frac{1}{2m\omega^2} = (n - \frac{1}{2})\hbar\omega + \frac{1}{2m\omega^2}
\end{aligned} \tag{40}$$

2.2 1D Harmonic Oscillator with $V_1 = x^4$

Again, we use the fact that $x = \frac{\sqrt{2}b^4}{2}(a^\dagger + a)$.

This means that:

$$x^4 = \frac{4b^4}{16}(a^\dagger + a)^4 \tag{41}$$

And the first order perturbation is:

$$\begin{aligned}
\langle n|V_1|n\rangle = \langle n|x^4|n\rangle &= \frac{b^4}{4}\langle n|(a^\dagger + a)^4|n\rangle \\
&= \frac{b^4}{4}(\langle n|aaa^\dagger a^\dagger|n\rangle + \langle n|aa^\dagger aa^\dagger|n\rangle + \\
&\langle n|a^\dagger aaa^\dagger|n\rangle + \langle n|a^\dagger aa^\dagger a|n\rangle + \langle naa^\dagger a^\dagger a||n\rangle + \langle n|a^\dagger a^\dagger aa|n\rangle) \\
&= \frac{b^4}{4}[(n+2)(n+1) + (n+1)^2 + 2(n+1)n + n^2 + n(n-1)] \\
&= \frac{\hbar^2}{4m^2\omega^2}(6n^2 + 5n + 3)
\end{aligned} \tag{42}$$

The fractional correction is thus just this perturbation divided by the total energy:

$$\begin{aligned}\text{Fractional Correction} &= \frac{\frac{\hbar^2}{4m^2\omega^2}(6n^2+5n+3)}{E_n+\frac{\hbar^2}{4m^2\omega^2}(6n^2+5n+3)} \\ &= \frac{\frac{\hbar^2}{4m^2\omega^2}(6n^2+5n+3)}{(n-\frac{1}{2})\hbar\omega+\frac{\hbar^2}{4m^2\omega^2}(6n^2+5n+3)}\end{aligned} \tag{43}$$

This shows that the correction is greater for greater values of n because this correction approaches 1 as $n \to \infty$.

2.3 Proton with Uniform density

Now we will exam a proton with a radius R where $R = 10^{-15}$meters. The charge is uniformly distributed charge with density:

$$\rho = \frac{e}{\frac{4}{3}\pi R^3} \tag{44}$$

We use Gauss' law to convert this to values for the electric field outside and inside the radius of the proton:

$$\int \vec{E} \cdot d\vec{A} = \frac{q}{\epsilon_0} \tag{45}$$

$$\begin{aligned}E4\pi r^2 = \frac{1}{\epsilon_0}\rho V &= \frac{e}{\frac{4}{3}\pi R^3\epsilon_0}\frac{4}{3}\pi r^3 \\ \implies E &= \frac{1}{4\pi\epsilon_0}\frac{er}{R^3} \quad r \le R\end{aligned} \tag{46}$$

$$\begin{aligned}E4\pi r^2 = \frac{1}{\epsilon_0}\rho V &= \frac{e}{\frac{4}{3}\pi R^3\epsilon_0}\frac{4}{3}\pi R^3 \\ \implies E &= \frac{1}{4\pi\epsilon_0}\frac{er}{r^2} \quad r \ge R\end{aligned} \tag{47}$$

Then we convert these electric field values into values for electric potential through $\vec{E} = -\vec{\nabla}V$. Then we multiply by another e to represent the potential energy of the proton:

$$\begin{aligned}V(r) &= \frac{1}{8\pi\epsilon_0}\frac{e^2r^2}{R^3} + C \quad r \le R \\ V(r) &= \frac{-1}{4\pi\epsilon_0}\frac{e^2}{r} + D \quad r \ge R\end{aligned} \tag{48}$$

The part of V where $r \ge R$ is the same as the unperturbed state because the proton "looks" the same as a point particle outside that radius and also $v(\infty) = 0$, meaning $D = 0$.

At radius R:

$$\frac{1}{8\pi\epsilon_0}\frac{er^2}{R^3} + C = \frac{-1}{4\pi\epsilon_0}\frac{e}{r}$$
$$\implies C = \frac{-3}{8\pi\epsilon_0 \frac{e}{R}} \tag{49}$$

Therefore the potential energy really looks like:

$$V(r) = \frac{1}{8\pi\epsilon_0}\frac{e^2r^2}{R^3} - \frac{3}{8\pi\epsilon_0\frac{e^2}{R}} \quad r \leq R$$
$$V(r) = \frac{1}{4\pi\epsilon_0}\frac{e^2}{r} \quad r \geq R \tag{50}$$

The perturbation that exists when $r \leq R$ comes from subtracting the perturbed and unperturbed ($V(r) = \frac{-1}{4\pi\epsilon_0}\frac{Ze^2}{r}$) potential energies:

$$V_1(r) = \frac{e^2}{4\pi\epsilon_0}\left(\frac{r^2}{2R^3} + \frac{1}{r} - \frac{3}{2R}\right) \quad r \leq R$$
$$V_1(r) = 0 \quad r \geq R \tag{51}$$

For the lowest energy state of hydrogen, $|n = 1, j = 0, m = 0\rangle$, which does not have any degenerate states, we find the first order correction by integrating in spherical coordinates like so:

$$\langle 100|V_1|100\rangle = \frac{e^2}{4\pi\epsilon_0}\int_0^{2\pi}\int_0^{\pi}\int_0^{R}\psi_{100}\left(\frac{r^2}{2R^3} + \frac{1}{r} - \frac{3}{2R}\right)\psi_{100}r^2 sin\theta dr d\theta d\phi$$
$$= \frac{e^2}{4\pi\epsilon_0}\frac{\mathrm{e}^{-\frac{R}{b}}\cdot\left(\left(12b^3 - 3R^2b + R^3\right)\mathrm{e}^{\frac{R}{b}} - 12b^3 - 12Rb^2 - 3R^2b\right)}{8\pi R^3 b}(2)(2\pi) \tag{52}$$

The states of $n = 2$ are all degenerate however, so we have to solve the following matrix based on perturbation theory:

$$\begin{pmatrix} \langle 200|V_1|200\rangle & \langle 200|V_1|21-1\rangle & \langle 200|V_1|210\rangle & \langle 200|V_1|211\rangle \\ \langle 21-1|V_1|200\rangle & \langle 21-1|V_1|21-1\rangle & \langle 21-1|V_1|210\rangle & \langle 21-1|V_1|211\rangle \\ \langle 210|V_1|200\rangle & \langle 210|V_1|21-1\rangle & \langle 210|V_1|210\rangle & \langle 210|V_1|211\rangle \\ \langle 211|V_1|200\rangle & \langle 211|V_1|21-1\rangle & \langle 211|V_1|210\rangle & \langle 211|V_1|211\rangle \end{pmatrix}\begin{pmatrix} a \\ b \\ c \\ d \end{pmatrix} = \mu_1\begin{pmatrix} a \\ b \\ c \\ d \end{pmatrix} \tag{53}$$

However, if we look at the potential it is clear that it only depends on are, meaning that for any particular $|njm\rangle$ we know that:

$$\langle nlm|V_1|n'l'm'\rangle = \int_0^{2\pi}\int_0^{pi} Y^*_{lm}Y_{l'm'}sin\theta d\theta d\phi \int_0^R R(r)^*V_1R(r)r^2dr$$
$$= \delta_{l,l'}\delta_{m,m'}(2)(2\pi)\int_0^R R(r)^*V_1R(r)r^2dr \tag{54}$$

The reason we can write it this way is we know that the perturbation V_1 is only dependent on r and not θ or ϕ. Thus we know that only the diagonal terms of our matrix could survive.

When it comes to our 4 diagonal states, we know that $l = 0$ the radial-dependent part of our wave function takes the form:

$$R(r)_{200} = \left(1 - \frac{r}{4b}\right) e^{\frac{-r}{4b}} \tag{55}$$

And for the $l = 1$ states it looks like:

$$R(r)_{21m} = \frac{r}{2b} e^{\frac{-r}{4b}} \tag{56}$$

For $|200\rangle$:

$$\langle 200|V_1|200\rangle =$$

$$\frac{e^2}{4\pi\epsilon_0}\frac{1}{\pi(4b)^3}\left[\frac{1344b^5 - 24R^2b^3 + 2R^3b^2}{R^3} - \frac{\left(2688b^5 + 1344Rb^4 + 288R^2b^3 + 36R^3b^2 + 3R^4b\right)\mathrm{e}^{-\frac{R}{2b}}}{2R^3}\right](4\pi)$$

$$= \frac{e^2b^2}{4^3R^3\pi\epsilon_0}(1344 - \frac{24R^2}{b^2} + \frac{2R^3}{b^3} + (-1344 - 672\frac{R}{b} - 144\frac{R^2}{b^2} - 18\frac{R^3}{b^3} - \frac{3}{2}\frac{R^4}{b^4})e^{\frac{-R}{2b}}) \tag{57}$$

Looking at this it is apparent that as $R \to 0$, the perturbation approaches $1344 - 1344 = 0$. If we plug in a value of $R = 10^{-15}$meters, we get a value of -2.295221796726887e-18 Joules for the perturbation

For $|210\rangle, |21-1,\rangle,$ and $|211\rangle$:

$$\langle 210|V_1|210\rangle = \langle 21-1|V_1|21-1\rangle = \langle 211|V_1|211\rangle$$

$$\frac{e^2}{4\pi\epsilon_0}\frac{1}{4\pi(4b)^3}\left[\frac{6b\mathrm{e}^{-\frac{R}{2b}}\cdot\left(\left(1920b^4 - 48R^2b^2 + 4R^3b\right)\mathrm{e}^{\frac{R}{2b}} - 1920b^4 - 960Rb^3 - 192R^2b^2 - 20R^3b - R^4\right)}{R^3}\right](\frac{4\pi}{3})$$

$$= \frac{e^2e^{\frac{-R}{2b}}b^2}{2\epsilon_0\pi4^3R^3}\left[(1920 - \frac{48R^2}{b^2} + \frac{4R^3}{b^3})e^{\frac{R}{2b}} - 1920 - 960\frac{R}{b} - 192\frac{R^2}{b^2} - 20\frac{R^3}{b^3} - \frac{R^4}{b^4}\right]$$

$$= \frac{e^2b^2}{2\epsilon_0\pi4^3R^3}\left[1920 - \frac{48R^2}{b^2} + \frac{4R^3}{b^3} - (1920 + 960\frac{R}{b} + 192\frac{R^2}{b^2} + 20\frac{R^3}{b^3} + \frac{R^4}{b^4})e^{\frac{-R}{2b}}\right] \tag{58}$$

Just like above, looking at this it is apparent that as $R \to 0$, the perturbation approaches $1920 - 1920 = 0$

Overall, the matrix representing the perturbation energies will look like:

$$\begin{pmatrix} \langle 200|V_1|200\rangle & 0 & 0 & 0 \\ 0 & \langle 21-1|V_1|21-1\rangle & 0 & \\ 0 & 0 & \langle 210|V_1|210\rangle & 0 \\ 0 & 0 & 0 & \langle 211|V_1|211\rangle \end{pmatrix} \begin{pmatrix} a \\ b \\ c \\ d \end{pmatrix} = \mu_1 \begin{pmatrix} a \\ b \\ c \\ d \end{pmatrix} \tag{59}$$

If we call this matrix A and take the determinant $|A - \lambda I|$ and set it to zero, we find the eigenvalues are:

$$\lambda = \langle 200|V_1|200\rangle, \langle 21-1|V_1|21-1\rangle, \langle 210|V_1|210\rangle, \text{ and } \langle 211|V_1|211\rangle \quad (60)$$

Each of these eigenvalues can correspond to these eigenvectors (not normalized):

$$\begin{pmatrix}1\\0\\0\\0\end{pmatrix}, \begin{pmatrix}0\\1\\0\\0\end{pmatrix}, \begin{pmatrix}0\\0\\1\\0\end{pmatrix}, \begin{pmatrix}0\\0\\0\\1\end{pmatrix} \quad (61)$$

Each of these eigenvalues represents the perturbation that corresponds to that particular eigenvector, which represents to one of the degenerate states (in the order represented in the matrix).

2.4 Applying an Electric Field to a Hydrogen Atom

We will think about how an electric field in the $\hat{k}$ direction will perturb a hydrogen atom:

$$\vec{E} = E\hat{k} \quad (62)$$

This electric potential corresponding to this field, causing a perturbation, will look like:

$$V_1 = eE_z = eErcos\theta \quad (63)$$

We will first understand the lowest energy hydrogen state $|100\rangle$ and $|200\rangle$. Both of these wave functions depend only on r and not θ or ϕ Therefore the θ integrals will go to zero because the functions inside are odd.

$$\begin{aligned}&\langle n=1,2, j=0, m=0|V_1|n=1,2, j=0, m=0\rangle \\ &= eE\int_0^\infty \int_0^\pi \int_0^{2\pi} \psi^2_{n=1,2,j=0,m=0}(r) r^3 cos\theta sin\theta dr d\theta d\phi = 0\end{aligned} \quad (64)$$

Now, we can look at the other two of the three $n = 2$ degenerate states. For these states it is also clear that for $\langle 21-1|V_1|21-1\rangle$ and $\langle 211|V_1|211\rangle$ the term inside the $d\theta$ integral will go to 0 because the functions inside the integrals will be periodic between 0 and π.

$$\langle 21\pm 1|V_1|21\pm 1\rangle = eE\int_0^\infty \int_0^\pi \int_0^{2\pi} \psi_{21,m=\pm 1}\psi_{21,\pm 1} r^2 cos\theta sin\theta dr d\theta d\phi \quad (65)$$

These two facts lead us to knowing the l values of the wave functions cannot be the same to have a perturbation on that state. Additionally, we know the m

values must be the same for their to be a perturbation because if they are not then the ϕ integral will go to zero because of $e^{\pm i\phi}$ part of the wave functions.

With this in mind we can form the matrix:

$$\langle nlm|V_1|nlm\rangle = \begin{pmatrix} 0 & -6eEb & 0 & 0 & & & & \\ 0 & 0 & 0 & 0 & -6eEb & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & & & & \end{pmatrix} \tag{66}$$

This matrix representing the perturbation can thus be diagonalized to find the new states after perturbation:

$$\begin{vmatrix} -\lambda & -6eEb & 0 & 0 \\ 0 & -\lambda & 0 & 0 \\ -6eEb & 0 & -\lambda & 0 \\ 0 & 0 & 0 & -\lambda \end{vmatrix} \tag{67}$$

This becomes:

$$\left[\lambda^2 - (-6eE)\right]\lambda^2 = 0 \tag{68}$$

So our eigenvalues are:

$$\lambda = 0, 0, -6eEb, 6eEb \tag{69}$$

We see that these two states, $|200\rangle$ and $|210\rangle$, have now been "mixed" and after applying a perturbation have been changed into being a mix of the both of them. these two mixed states (once normalized) are understood like so:

$$|mixed\,1\rangle = \frac{1}{\sqrt{2}}[|200\rangle - |210\rangle] \tag{70}$$

$$|mixed\,2\rangle = \frac{1}{\sqrt{2}}[|200\rangle + |210\rangle] \tag{71}$$

Where mixed 1 corresponds to $V_1 = 6eEb$ and mixed 2 corresponds to $V_1 = -6eEb$. So one of these mixed states is higher energy due to the perturbation and the other is lower energy. No longer are there 4 degenerate states for n=2 but rather 2 degenerate states and these 2 other mixed states.

This hybrid states corresponds to a 2s and 2p orbital, and this concept might have parallels to how bonding creates sp hybridizations, with the electrons in the bonds acting as the electric field that causes a Stark effect that accounts for changes in the states of the electrons.

The Hydrogen Atom

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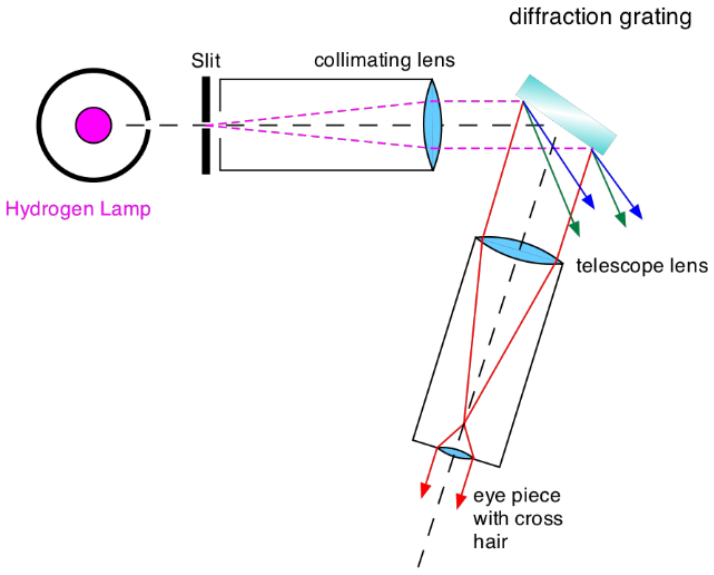
Contents

1 The Experiment

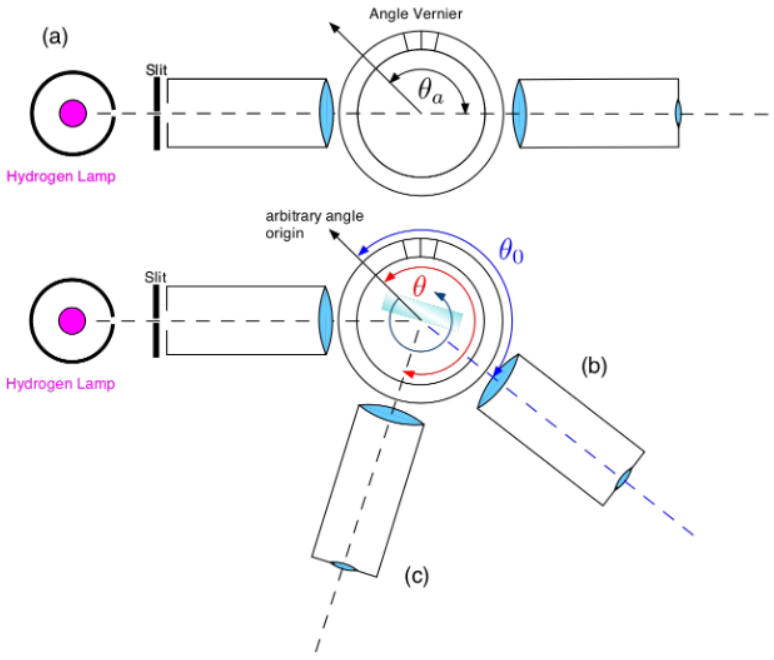
1.1 Introduction

A hydrogen lamp was placed with a current running through it, providing it with energy. This causes the hydrogen lamp to emit light. The quality of the light emitted from this lamp is investigated by splitting up the wavelengths it emits through use of a diffraction grating which reflects the light at various angles. The wave- like nature of light means that in certain locations, there will be constructive interference and the light will be visible very clearly.

If there are only certain wavelengths of light visible, then this may be explained through the the idea of only quantized packets of light being able to be emitted, which would each correspond to only a certain wavelength of light, through the transition of a electrons from a higher to lower energy state. This transitions and the energy loss associated with it would thus correspond to the energy and thus wavelengths of the photons being emitted by the hydrogen lamp.



The optical axis angle (θ_a) of the hydrogen lamp, shown as (a) in the figure below, the angle of the "0^{th} image" (θ_0), shown as (b) below, and every angle of the various wavelengths of light, represented as (c) in the figure below, must be measured.



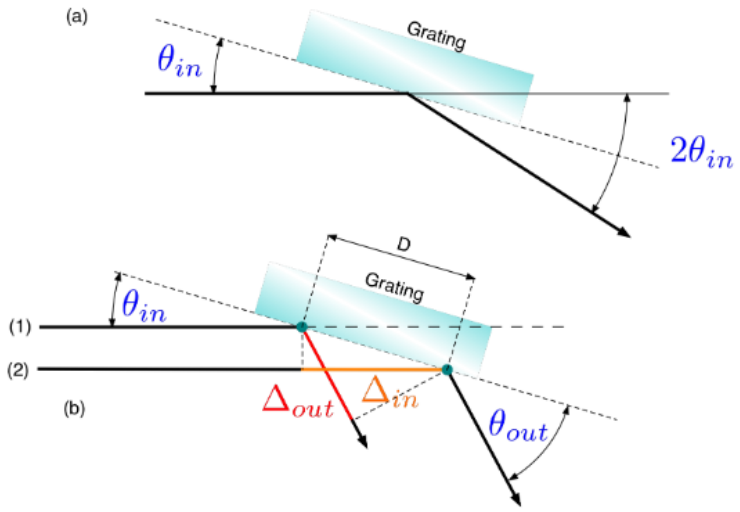
1.2 Wavelength and Energy Calculations

These angle values are used to find a value for wavelength at each location. First, the measured angles are converted into values for the incident angle (θ_{in}) and the outgoing angle (θ_{out}):

$$\theta_{in} = \frac{\theta_0 - \theta_a}{2} \tag{1}$$

$$\theta_{out} = \theta - (\theta_a - \theta_{in}) \tag{2}$$

These angles are used to find the difference in path-length between two vectors of light hitting the diffraction grating at two different locations on the grating. Here, D is the distance between locations on the diffraction grating and is called the grating constant for the particular diffraction grating.



Each of these path-length differences is found by looking at the geometry:

$$\Delta_{in} = Dcos(\theta_{in}) \tag{3}$$

$$\Delta_{out} = Dcos(\theta_{out}) \tag{4}$$

Therefore, the total distance in the path between these rays is:

$$\Delta_{total} = \Delta_{in} - \Delta_{out} = Dcos(\theta_{in}) - Dcos(\theta_{out}) \tag{5}$$

In order for the light to be visible, the rays must be constructive, meaning the difference in the path-length of the rays must be an integer of the wavelength of the light:

$$\Delta_{total} = m_d\lambda \tag{6}$$

$$m_d = 0, \pm1, \pm2, \pm3, ... \tag{7}$$

Therefore wavelength is described as:

$$\lambda = \frac{Dcos(\theta_{in}) - Dcos(\theta_{out})}{m_d} \tag{8}$$

These wavelengths can be converted to an energy value through the use of some constant, which we theorize to be Planck's constant. This constant converts the frequency of the light into a value for energy in Joules:

$$E = \frac{hc}{\lambda} \tag{9}$$

This can now be expanded on further by theorizing on the form and use of so-called wave functions that describe the electron in the hydrogen atom (and thus dictate the energies/wavelengths of the emitted photons). Further detail on this will now be provided.

1.3 Introduction to Wave Functions

Wave functions can be written in terms of functions of their separate spherical coordinates as follows:

$$\psi_{n,j,m} = R_{n,j}(r)P_j^m(\theta)e^{im\phi} \tag{10}$$

Where n is a quantum number related to the total energy, j is related to the angular momentum, and m is related to the projection of the angular momentum.

Written in detail, these wave functions are in the form:

$$\psi_{n,j,m} = \sum_{k=0}^{\infty} C_k \left(\frac{r}{b}\right)^k e^{\frac{-r}{2bn}} r^j P_j^m(\theta)e^{im\phi} \tag{11}$$

To find values of $\sum_{k=0}^{\infty} C_k \left(\frac{r}{b}\right)^k$, first we need to know how many of these constants are nonzero for a state. So, we define some P which is the upper limit of k. We find this P to be related to n and j through $P = n - j - 1$.

Furthermore, we will find in this chapter that the relationship between constants is the following, allowing us to put all the constants in terms of the lowest constant C_0, which can then be found through normalization:

$$C_{k+1}\frac{\frac{1}{n}(k+j+1)-1}{(k+1)(k+2j+2)}C_k \tag{12}$$

The P_j^m functions can be found for different m's by starting off with the largest or smallest value of m possible for a given j and then using the relationship below to find the functions for the rest of the states of that j:

$$P_j^j = P_j^{-j} = N_j[sin\theta]^j \tag{13}$$

$$\left(\frac{\partial}{\partial\theta} - mcot\theta\right) P_j^m(\theta) = \sqrt{j(j+1) - m^2 - m}P_j^{m+1} \tag{14}$$

We find that the part of the wave function that is dependent on the angles θ and ϕ, in other words $P_j^m(\theta)$ and $e^{im\phi}$ was understood through using the angular momentum operators. However, the radial part of the wave function and in particular the sum $\sum_{k=0}^{\infty} C_k \left(\frac{r}{b}\right)^k$ was found by inserting a potential energy into the wave equation, in this case the potential of a hydrogen atom, which is dependent on r.

We will now go into detail about how this way of writing the wave function came about.

1.4 Hydrogen Atom Potential and How It Alters the Wave Functions

Through experiment, the potential of a hydrogen atom has been found to be:

$$V(r) = \frac{-1}{4\pi\epsilon_0}\frac{Ze^2}{r} \tag{15}$$

Where ϵ_0 is the permittivity of free space, Z is the atomic number (1 in the case of hydrogen), and e is the charge of an electron.

In order to apply this potential to the previous setup, we will convert to natural units. So, we will set b as the following in order to convert r to natural units as in:

$$r = bu \tag{16}$$

$$\frac{2m}{\hbar^2}\frac{Ze^2}{4\pi\epsilon_0}b = 1 \tag{17}$$

And by plugging in all these constants and rearranging for b we arrive at:

$$b = 2.64588603 \times 10^{-11} \text{ meters} \tag{18}$$

We see that the units of $\frac{2mb^2}{\hbar^2}$ are Joules, meaning for natural units of energy we can set:

$$E = \frac{-\hbar}{2mb^2}\beta^2 \tag{19}$$

Our energy equation was:

$$\frac{d^2\psi_{E,j}(r)}{dr^2} + \frac{2(j+1)}{r}\frac{d\psi_{E,j}(r)}{dr} + \frac{2m}{\hbar^2}[E - V(r)]\psi_{E,j}(r) = 0 \tag{20}$$

So our energy equation in natural units becomes:

$$\frac{d^2\chi_{E,j}(u)}{du^2} + \frac{2(j+1)}{u}\frac{d\chi_{E,j}(u)}{du} - \beta^2\chi_{E,j}(u) + \frac{1}{u}\chi_{E,j}(u) = 0 \tag{21}$$

By examining the limit as $u \to \infty$ we find that $\frac{d^2\chi_{E,j}(u)}{du^2} \sim \alpha\chi_{E,j}(u)$ and thus $\chi_{E,j}(u) \sim e^{-\beta u}$ and so we rewrite $\chi_{E,j}(u)$ as:

$$\chi_{E,j}(u) = e^{-\beta u}R_{E,j}(u) \tag{22}$$

Where $R_{E,j}(u)$ is a polynomial:

$$R_{E,j}(u) = \sum_{k=0}^{\infty} c_k u^k \tag{23}$$

This ultimately results in (12) being rewritten as:

$$\sum_{k=0}^{\infty}\{[2(j+1)(k+1)+k(k+1)]c_{k+1} + [(-2\beta)k + (1-2(j+1)\beta)]c_k\}u^k = 0 \tag{24}$$

Since each of these terms in the sum must be 0 in order for the total sum to be 0, we know that the coefficient of each term must be 0, resulting in the recursion relation:

$$C_{k+1} = \frac{2\beta(k+j+1)-1}{k(k+1)+2(j+1)(k+1)} \tag{25}$$

Furthermore, we know that the polynomial $R_{E,j}(u)$ must terminate because $\chi_{E,j} \to 0$ as $u \to \infty$ (due to normalizability conditions). So there must be some value of k, which we will call P, for which:

$$2\beta(P+j+1)-1=0 \tag{26}$$

We can rearrange for a value of β (energy):

$$\beta = \frac{1}{2(j+P+1)} = \frac{1}{2n} \tag{27}$$

So, our solutions depend on 3 quantum numbers:

$$\begin{aligned} &n = 1, 2, 3, ... \\ &j = 0, 1, 2, ... \\ &m = -j, -j+1, .., j-1, j \end{aligned} \tag{28}$$

(And P is a result of a choice of a particular j and n):

$$P = n - j - 1 \tag{29}$$

We have been working in natural units but also, of course, if we want, we can always bring our wave function back to units of r, in which case it would look again like this:

$$\psi_{n,j,m}(r,\theta,\phi) = \left(\sum_{k=0}^{\infty} c_k \left(\frac{r}{b}\right)^k\right) e^{-\frac{r}{2bn}} r^j P_j^m e^{im\phi} \tag{30}$$

2 Data

2.1 Wavelength/Energy at Each Data Point

These are the values for wavelength and energy at each angle data point, computed from equation (8) and (9).

Values of Wavelength and Energy when m_d=1		
	Wavelength (nm)	Energy (eV)
Red	654.9 +/- 1.6	1.893 +/- 0.005
Green-Blue	486.0 +/- 1.5	2.551 +/- 0.008
Violet	428.0 +/- 1.5	2.897 +/- 0.010
Dark Violet	413.8 +/- 1.4	2.996 +/- 0.010
Values of Wavelength and Energy when m_d=2		
	Wavelength (nm)	Energy (eV)
Red	656.2 +/- 0.7	1.890 +/- 0.002
Green-Blue	485.5 +/- 0.8	2.554 +/- 0.004
Violet	433.7 +/- 0.8	2.859 +/- 0.005
Dark Violet	409.6 +/- 0.8	3.027 +/- 0.006
Values of Wavelength and Energy when m_d=3		
	Wavelength (nm)	Energy (eV)
Green-Blue	485.91 +/- 0.36	2.552 +/- 0.002
Violet	433.56 +/- 0.45	2.860 +/- 0.003

2.2 Final Wavelength and Energy Values

Using these values, we can find the weighted mean and uncertainty of each wavelength and energy, as described in the data analysis section:

Weighted Mean Values of Wavelength and Energy for Each Wavelength		
	Wavelength (nm)	Energy (eV)
Red	655.99 +/- 0.62	1.890 +/- 0.002
Green-Blue	485.85 +/- 0.32	2.552 +/- 0.002
Violet	433.21 +/- 0.38	2.862 +/- 0.003
Dark Violet	410.66 +/- 0.72	3.019 +/- 0.005

3 Conclusions of the Experiment

4 Connecting back to our lecture

We had designated β to in essence be what defines our natural unit of energy where:

$$E = \frac{-\hbar^2}{2mb^2}\beta^2 = \frac{-Z^2e^4m}{8\pi^2\epsilon_0^2\hbar^2}\beta^2 = \frac{-Z^2e^4m}{32\pi^2\epsilon_0^2\hbar^2n^2} \tag{31}$$

(Remember we found set found that $\beta = \frac{1}{2(j+P+1))}$ and set this to $\beta = \frac{1}{2n}$)
This E is the total kinetic energy of the electron in a given state.
For the electron on a hydrogen atom this simplifies to:

$$E_n = \frac{-e^4m_e}{32\pi^2\epsilon_0^2\hbar^2n^2} \tag{32}$$

In the experiment, we look at the Balmer series, meaning transitions from n=3,4,5,6... down to n=2. So the wavelengths coming from the hydrogen lamp

would have the energy of these transitions. For example, for the transition from n=3 to n=2:

$$E_3 - E_2 = \frac{-e^4 m_e}{32\pi^2 \epsilon_0^2 \hbar^2} \left(\frac{1}{3^2} - \frac{1}{2^2} \right) \tag{33}$$

And for any other transition down to n=2 we find that:

$$E_n - E_2 = \frac{-e^4 m_e}{32\pi^2 \epsilon_0^2 \hbar^2} \left(\frac{1}{n^2} - \frac{1}{4} \right) \tag{34}$$

For these constants:

$$\begin{aligned} \epsilon_0 &= 8.8541878128 \times 10^{-12} \frac{C^2 s^2}{kgm^3} \\ \hbar &= 1.054571817 \times 10^{-34} \frac{kgm^2}{s} \\ e &= 1.602176634 \times 10^{-19} C \\ m_e &= 9.1093837015 \times 10^{-31} kg \end{aligned} \tag{35}$$

So the photon energies emitted by Balmer series transition are defined by:

$$\begin{aligned} E_\gamma = E_n - E_2 = \frac{-e^4 m_e}{32\pi^2 \epsilon_0^2 \hbar^2} \left(\frac{1}{n^2} - \frac{1}{4} \right) &= -13.6 \left(\frac{1}{n^2} - \frac{1}{4} \right) \text{ eV} \\ &= 2.17987236 \times 10^{-18} \left(\frac{1}{4} - \frac{1}{n^2} \right) \text{ Joules} \\ &= 2.17987236 \times 10^{-18} * \left(\frac{6.241509 \times 10^{18} \text{ eV}}{\text{J}} \right) \left(\frac{1}{4} - \frac{1}{n^2} \right) \\ &= 13.60569 \left(\frac{1}{4} - \frac{1}{n^2} \right) \text{ eV} \end{aligned} \tag{36}$$

The first four transitions would be:

$$n_{initial} = 3 : \; E_3 - E_2 = 13.60569 \left(\frac{1}{4} - \frac{1}{9} \right) \text{ eV} = 1.889680 \text{ eV} \tag{37}$$

$$n_{initial} = 4 : \; E_4 - E_2 = 13.60569 \left(\frac{1}{4} - \frac{1}{16} \right) \text{ eV} = 2.551067 \text{ eV} \tag{38}$$

$$n_{initial} = 5 : \; E_5 - E_2 = 13.60569 \left(\frac{1}{4} - \frac{1}{25} \right) \text{ eV} = 2.857196 \text{ eV} \tag{39}$$

$$n_{initial} = 6 : \; E_6 - E_2 = 13.60569 \left(\frac{1}{4} - \frac{1}{9} \right) \text{ eV} = 3.023487 \text{ eV} \tag{40}$$

This experiment provides evidence for the ideas, mathematics, and theory behind quantum mechanics and the quantization of the energy states of an electron. It also confirms that the wavelengths observed are coming from the Balmer Series visible wavelengths of Hydrogen because the values are very close to the literature and computed values and the experimentally determined Rydberg constant is accurate when assuming these are Balmer series wavelengths (how the Rydberg constant was determined experimentally was not presented here). Additionally, most of the Balmer Series includes visible wavelengths, which is what was seen experimentally.